CELLULOID

ITS RAW MATERIAL, MANUFACTURE, PROPERTIES AND USES

DR. FR. BÖCKMANN

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CELLULOID

CELLULOID

ITS RAW MATERIAL, MANUFACTURE, PROPERTIES AND USES

A HANDBOOK FOR MANUFACTURERS OF CELLULOID AND CELLULOID ARTICLES, AND ALL INDUSTRIES USING CELLULOID; ALSO FOR DENTISTS AND TEETH SPECIALISTS

BY

Dr. Fr. BÖCKMANN

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PREFACE TO THE FIRST EDITION.

After experimenting for a number of years Hyatt succeeded in preparing a new substance, Celluloid, from camphor and gun-cotton, on a manufacturing scale; and the valuable properties of this substance soon brought it into public favour.

Envious competitors soon spread a rumour that celluloid was liable to explode and was inflammable in the highest degree; and sensational reports of this kind circulated in the daily and technical press almost unchallenged. Each and every busybody felt, and even now feels, justified in wasting the space of the daily papers with a "communication" or a letter "On the Inflammability of Celluloid". In these "communications" we read the most amazing accounts of ladies whose hair has been burnt off by the ignition of a celluloid comb: of celluloid billiard balls set on fire by contact with burning cigars: of combs lying near a *cafetière*, and set on fire by a drop of burning spirit: of flames a yard high shooting out from some celluloid ornament that has been brought near a light: of the impossibility of extinguishing burning celluloid, etc., etc.

However amusing such accounts may be to the expert, they produce anxiety in the minds of the general public; and it is one of the chief purposes of the present work to put an end to such nonsense, and afford the public a clear insight into the properties of celluloid.

The manufacture, properties and technical utilisation of celluloid are exhaustively treated, so that it is hoped the book will meet with a good reception from those practically interested in the subject.

In many cases celluloid is still regarded with anxiety from the fact that gun-cotton is used in its manufacture. On this account an attempt has been made in the sections dealing with the nitro-celluloses in general, gun-cotton and collodion wool, to make the public acquainted with the properties of these explosives, and thus correct the overdrawn statements made in this connection.

Moreover, the author has endeavoured to confine himself to actualities, and give the actual conditions obtaining in practice. That he has succeeded in doing this in every case is, however, doubtful, in view of the great difficulty of obtaining reliable information on many points that are regarded as trade secrets.

The author, therefore, ventures to hope that both the expert, the press and the public will be able to derive benefit and instruction from his labours. His greatest pleasure, however, would be to know that he had done something to remove the erroneous ideas prevailing on the subject of cellulose, and thus help this greatly maligned and misunderstood substance to regain its rights, as it will do sooner or later.

PREFACE TO THE THIRD EDITION.

SINCE the appearance of the previous editions the applications of celluloid have been considerably extended, whilst the method of manufacture has remained almost unchanged. Continuous attempts have been made to replace camphor by other suitable materials, and also to diminish the inflammability of the product—a result that would be highly beneficial in certain spheres of application. Notwithstanding the small space available, all these novelties have been fully dealt with, so that the present edition is up to date, and will be found to meet all requirements and be useful to a large circle of readers.

1907.

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INTRODUCTION.

THE progress of civilisation, and the increasing requirements of all branches of trade and industry, have been accompanied by a growing scarcity of many raw materials, the prices of which have risen in consequence. For this reason numerous attempts have been made, for some considerable time past, to imitate certain raw materials, on the one hand, and on the other, to find other materials capable of replacing them for many purposes if not in all. Thus, endeavours have been made to imitate ivory and caoutchouc in the first place; then tortoise-shell, horn, amber, etc., the earliest success in this direction being that obtained by Parkes of Birmingham, with the substance known as Parkesine, and used as a substitute for ivory and caoutchouc. This substance, which, while as hard as horn, is as flexible and supple as leather, and is capable of replacing ivory and mother-of-pearl as well as caoutchouc and guttapercha, was the first of its kind to arouse general interest.

Parkesine is interesting as the forerunner of celluloid, and its preparation and application must therefore be dealt with. The inventor prepared it by mixing anhydrous wood naphtha with gun-cotton, and thus obtained a solution suitable, according to its consistency, for purposes ranging from waterproof clothing to the insulation of telegraph wires, manufacture of tubes, etc. To ameliorate the hardness and brittleness, which unfitted it for certain uses, the product was kneaded with castor oil, cotton-seed oil, or other fatty oils, a mixture of the gun-cotton solution and castor oil, for instance, furnishing a compo specially adapted for coating telegraph wires and waterproofing textile fabrics.

Subsequently improvements were introduced, consisting in the employment of collodion dissolved in wood spirit and mixed with sulphonated drying oils, according to the degree of elasticity required, from 2 to 10 per cent. of sulphur chloride, together with an addition of carbon disulphide to check the violence of the reaction, the resulting product being incorporated with varying proportions of dissolved gun-cotton, according to the result desired, but seldom more than 20 per cent. By warming, the mass is converted into a pasty condition, enabling it to be moulded into any desired shape. The products obtained in this way were very handsome, and included sheets in various colours, imitation marble patterns, combs, knife handles, etc. The solvent employed facilitated the introduction of various colouring agents (coal-tar dyes in particular) into the mass; and powdered colours could also be incorporated by rolling or kneading.

For some years Parkesine enjoyed a fair amount of popularity in England, but was too expensive to retain that position long; and it was not until 1869 that the invention of celluloid by the brothers Hyatt, who were printers at Newark in the State of New Jersey, opened up a new era to this class of preparations. The new discovery was arrived at in the course of experiments concerned in the production of a printer's roller material capable of withstanding atmospheric influences. The experiments were made with collodion, and it was found that by suitably treating this substance with camphor an entirely new product, possessing very valuable properties, was obtained. The name celluloid was given to it on account of the cellulose forming the raw material.

Though in the first edition of this work a future was foretold for this product, it could not be foreseen at that time that it would develop into such an important industry as it has since done. It may possess a certain amount of interest to reproduce in this place a few of the opinions expressed at the earlier stages of the celluloid industry.

Thus, the brothers Dobler, makers of hard rubber and celluloid articles in Berlin, stated their belief that the good qualities of celluloid would be of but little avail, owing to the unreasonable prejudice against it and the half-hearted attempts made to introduce it into the various branches of industry, so that it was looked on as overrated. It was also rendered unpopular by newspaper articles instigated by competing interests and containing foolish statements put forward with the greatest seriousness, the effect being the greater since these assertions were also disseminated by leading journals and even by trade organs. One of these statements was to the effect that "the idea that there is any future at all for celluloid is now banished from the minds of manufacturers and traders".

Another firm of celluloid makers gave a more favourable opinion, having written to the author as follows: "It is possible that celluloid will not retain its present popularity, more especially in view of the undiminished agitation against it on the part of interested persons; but it will never, as is often prophesied, entirely disappear, its prominent position along with ivory, tortoise-shell, hard rubber, etc., being assured". Professor Reuleaux, however, held opposite views. He averred that "It is unnecessary to employ this substance for purposes of imitation in order to render it popular. As a matter of fact, celluloid needs handling very carefully in connection with industrial art. It would only be too easy to deviate with this new substance into the by-path of imitation, that insidious evil which has already done so much injury to our industries that friends of industrial art shudder when they hear of a new 'successful imitation' being introduced. German manufacturers cannot be too urgently warned against this habit of imitation, which is always attended with the danger that what is really capable of accomplishment is lost sight of in attempts after the unattainable. If we wish to make a good article, we must strive after the truth and not after imitations: that is to say, given a good material, we should endeavour in its industrial application, to develop it to the extent which its inherent properties permit. In this way we shall obtain better results than by imitation, which at best always retains a certain inferiority."

Against this view, which contains a good deal of truth, must be set the fact that the materials to be imitated are so expensive that they are not within the means of all. In any case, however, in connection with the endeavours to obtain good imitations by means of celluloid, it should not be forgotten that this substance is of itself excellently adapted for utilisation, without any resort to borrowed plumes.

More than twenty years ago the high price of celluloid, owing to the imperfect methods of manufacture, imposed certain limits on its use, and in many cases rendered the employment of natural products more practicable. At the present time the conditions are different, owing, on the one hand, to increased competition, and on the other, to improved methods of manufacture. The production of imitations by means of celluloid at that time was less with the idea of competing with individual materials than to show what celluloid could do. Nowadays the production of certain imitations is justified, if only for the reason of their extreme cheapness, and because they can be made in a far simpler manner than is possible in the case of many genuine materials.

For many branches of industry celluloid has become a really indispensable product, and one capable of extensive application.

The main objection at one time existing against the widespread use of celluloid was its inflammability and the rapidity with which it burns when brought near a flame. This, however, is the case with other materials, and it might be said, for instance, that no lady should wear a dress made of such inflammable material as muslin.

Many lives have been sacrificed through the ignition of ladies' dresses, but no case is on record of lives being lost in this way through celluloid articles properly used; and, moreover, these articles are very small and not used as clothing.

The only time celluloid can take fire is when it is brought into direct contact with flame, or has been heated to such an extent as to give off inflammable vapours; and even then the presence of a flame is necessary to cause these vapours to ignite, or some special cause, such as the sudden admission of air, produces an explosion of a large volume of celluloid vapour.

The story about a billiard-ball that was ignited by contact with a lighted cigar lying on the edge of the table, and that set fire to the cloth before it could be removed by means of tongs, is a fable, and impossible, as can be proved by trying the effect of a lighted cigar on celluloid.

Vapours that have been liberated from celluloid by contact with a glowing body will ignite on the approach of a flame, and the latter will then also attack the object, as in the case of a celluloid cigar-holder when the cigar has burned down into the holder.

Burning celluloid can be easily extinguished by a single strong puff of wind, unless the burning object has been on fire for some time. If a flame has just commenced to light a piece of paper, the latter can be blown out with ease; but if the whole of the paper has been attacked, blowing is no longer of any use. The same applies in the case of celluloid or any other burning object.

If the concentrated heat of a flame is allowed to act on celluloid, as will be the case when the latter is held over a petroleum lamp, the celluloid will ignite at a distance of about eight inches above the top of the lamp chimney. This is not surprising, as a piece of paper held in the same position will turn brown and give off a cloud of smoke. Under these conditions the celluloid first gives off vapours, and then emits a slight, barely audible crackling noise.

Immediately, a small flame appears twice in succession just above the surface of the celluloid, and the next moment the mass takes fire. In this case it is not the celluloid itself but the vapour that ignites, the flame then attacking the celluloid. Exactly the same thing can be observed with wood, though no one would think of raising objection to the use of wooden utensils on that account. Wood is a well-known material, whereas celluloid is comparatively new; and it is easy to understand that the opponents of this new product should desire to emphasise its defects and keep silent on the subject of its advantages.

From what has been said, it will be evident that celluloid articles can only be ignited when they are held in a flame or have been heated sufficiently highly to decompose the material. Therefore, wearers of celluloid articles should take care not to go too near a flame, not from dread of the celluloid burning, but chiefly because of the risk of the hair or other parts of the body taking fire.

In any event, care should be exercised in selecting articles made of celluloid, as cigar or cigarette-holders of this material may be really dangerous, owing to the ease with which it is decomposed in contact with the glowing tobacco when the latter is allowed to burn down too far. Should this result ensue, there is danger of the lips and mouth being scorched by the hot vapours.

Particular care is necessary when celluloid is stored in large quantities, and when the material is being worked in the lathe, etc. Some time ago a number of fires broke out at short intervals in celluloid stores and workshops, and the cause was attributed, in the former especially, to the liberation of celluloid vapours, though this could not be proved; and indeed it is hardly likely that, even with large quantities of celluloid, a sufficient volume of vapour would be liberated as to ignite explosively on a sudden irruption of air.

The case is different in workshops where celluloid is being worked, the fine dust given off filling the air of the room and forming a source of danger in view of the inflammable character of the material and the explosive nature of certain kinds of dust (*e.g.*, flour in flour mills).

In the course of years the public has gradually learned that celluloid is not really more dangerous than many other articles in general use; and the best proof of this is the widespread application of this substance for many articles of use, toilet articles, etc., and also for industrial purposes. If there were any risk, or any danger greater than we are exposed to daily, celluloid would not have succeeded in making such a way for itself as it has now done.

Moreover, in the course of the last few years, innumerable methods have been proposed for replacing the expensive ingredient, camphor, by uninflammable materials, and both in this and other ways, to introduce substances capable of greatly diminishing (if not entirely removing) its inflammability, and thereby considerably lessening the risks attending the storage, working and use of celluloid. Finally, there are now in the market materials, like galalith from milk casein, that have all the appearance of celluloid and are quite uninflammable.

CHAPTER I.

RAW MATERIALS FOR THE MANUFACTURE OF CELLULOID.

Celluloid may in general—or at least it could until quite recently—be described as a composition consisting of more or less nitrated pure cellulose and camphor, dissolved in various solvents, mechanically treated, stained any desired colour with dyestuffs or pigments, and obtained, after the evaporation of the solvents, in the form of solid blocks, plates, sheets and rods, which are worked up into all manner and sizes of useful articles. The manufacturers of celluloid, who are comparatively few in number, restrict themselves to producing this material (and xylonite), whereas the numerous makers of celluloid articles work up the product by moulding, pressing or lathe turning.

Before going into the manufacturing process, which has undergone extensive modification through the introduction of substances intended to supersede camphor to a greater or smaller extent, we will first treat of the raw material, cellulose and its products, and nitro-cellulose (gun-cotton, collodion) so far as is necessary to make the subject understandable.

Cellulose and Pyroxylin.

The chief constituent of the organs of trees, and all other vegetable growths whatsoever, is the substance known as cellulose, from the fact that it constitutes the material of the cell walls and tissues.

Perfectly pure cellulose, unmixed with any other substance, is never met with in nature, but is always more or less firmly combined with colouring matters, fats, albuminoids or gummy substances. In the younger parts of plants it is fairly pure, but wood and the ligneous portions of plants contain cellulose in admixture with extraneous bodies, more particularly encrusting or mineral matters.

Cotton and paper made from rags (especially Swedish filter paper) may be regarded as fairly pure cellulose, and the prepared fibres of flax and hemp also contain it in a nearly pure state.

Cellulose is distinguished by its high power of resisting most chemical reagents, being insoluble in water, alcohol, ether, fatty and volatile oils, and even in dilute acids and alkalis. The only known chemical compound in which it is completely soluble without decomposition is ammoniacal copper oxide solution prepared by dissolving freshly precipitated copper hydroxide in highly concentrated ammonia. Cellulose (cotton or filter paper) introduced into this deep blue liquid swells up to a viscous mucilage, and then gradually dissolves to a blue mass, which forms a coherent film when spread out in thin layers to dry.

Perfectly pure cellulose is prepared by treating cotton, purified flax or hemp fibres (fabrics), or pure, unsized paper with dilute hydrochloric acid, hydrofluoric acid and chlorine water in succession, then with dilute alkalis, and finally with alcohol, ether and water. These solvents successively extract the impurities from the cellulose, and leave the latter in a pure, or nearly pure, state. Concentrated sulphuric acid or hydrochloric acid will chemically modify cellulose and dissolve it; and by boiling cellulose with dilute hydrochloric or sulphuric acid, it is converted into grape sugar.

Paper treated with, or dipped in, a mixture of one part by volume of sulphuric acid and half that quantity of water, for one to two minutes, and then washed quickly with plenty of water, furnishes parchment paper, which no longer separates into its individual fibres when placed in water.

If cellulose be treated with a mixture of concentrated nitric acid and sulphuric acid, it undergoes alteration into a number of compounds known under the generic name of nitro-cellulose. As a rule these bodies exhibit the properties of gun-cotton; but in certain circumstances, and especially when weaker nitric acid has been used, or saltpetre has been employed instead, a nitro-cellulose is formed which differs from gun-cotton in being less explosive (though it burns very rapidly) and also by being soluble in a mixture of ether and alcohol. This solution is generally known as collodion, the fairly innocuous dissolved nitro-cellulose therein constituting collodion cotton.

The practical preparation of chemically pure cellulose being a difficult and expensive process, the pure material is dispensed with, being replaced by substances containing cellulose, such as cotton, paper, linen, etc. Despite the innumerable recipes and patents for preparing cellulose from various other materials, alleged to be specially adapted for the production of nitro-cellulose for this purpose, it is doubtful whether any other materials than cotton, paper and linen have ever been used on a practical scale. The cellulose recovered from the wood of coniferous trees might come under consideration for this purpose, but the suitability of one or the other kind of cellulose will have already been carefully threshed out by the manufacturers of celluloid, by practical trials or on theoretical grounds, and it may be definitely stated that cotton, paper and linen are the only raw materials, containing cellulose, actually employed.

As already mentioned, the nitro-celluloses are prepared by treating substances containing cellulose with a mixture of concentrated sulphuric acid and more or less concentrated nitric acid. The sulphuric acid, which plays no part in the actual conversion process, serves exclusively for absorbing the water liberated by the action of the nitric acid on the cellulose, so as to prevent a too rapid dilution and premature weakening of the nitric acid.

In addition to cellulose many other organic substances are converted by nitric acid into nitro-compounds, or "nitrated," the action consisting in the nitric acid being split up into a nitric acid radicle (the so-called nitro-group or hyponitric acid) and a water radicle. The nitric radicle combines chemically with the organic substance present, which it "nitrates," whilst the water radicle unites with hydrogen, eliminated from the organic substance, to form water, which is immediately seized by the sulphuric acid.

The actual nitro-compound formed depends on the strength of the nitric acid, the length of the reaction and the temperature of the acid mixture, as well as on the nature of the cellulose material used. The nitro-group may combine two, three, four, five or six times with the cellulose, and furnish the following compounds:—

Dinitro-cellulose,	containing	2	nitro-groups.
Trinitro-cellulose	,,	3	,,
Tetranitro-cellulose	,,	4	,,
Pentanitro-cellulose	,,	5	,,
Hexanitro-cellulose	,,	6	,,

The nitro-cellulose known as gun-cotton, and now used as the propulsive agent in modern ammunition almost exclusively, is the most highly nitrated product of the series, hexanitro-cellulose. All the others are collodion wools, differing from gun-cotton in that they are soluble in a mixture of ether and alcohol, with which they form the liquid known as collodion.

One or other of these nitro-celluloses forms the main product of nitration, according to the manner in which the operation is performed; but it should be noted that other members of the series are formed at the same time. Thus commercial gun-cotton contains collodion wool nitro-celluloses; whilst a collodion wool consisting chiefly of tetranitro-cellulose, for instance, will contain other members of the series, *e.g.*, trinitro-cellulose. It is true that, by working on a laboratory scale and by prolonged washing with ether-alcohol, gun-cotton can be obtained in the pure state; but, on the other hand, it is only with great difficulty, if at all, that a collodion wool can be prepared that contains only a single nitro-cellulose and not a mixture. The five nitro-celluloses are formed under the following conditions:—

1. Hexanitro-cellulose (gun-cotton) is formed by the action of a mixture of concentrated nitric acid (sp. gr. 1·5) and pure concentrated sulphuric acid (66° B.) on a substance containing cellulose. The proportions of the two acids may be varied considerably: for instance, three volumes of nitric acid (sp. gr. 1·517) to one of sulphuric acid (sp. gr. 1·84), or three volumes of sulphuric acid (sp. gr. 1·845) to one of nitric acid (sp. gr. 1·5). In either case a nearly chemically pure gun-cotton is obtained. For further particulars as to the process, see under Gun-cotton.

2. Pentanitro-cellulose is always formed when cotton is acted on by highly concentrated acid mixtures at a low temperature. Its production is facilitated by a high proportion of sulphuric acid in the mixture, but it is never obtained pure, being always accompanied by either hexanitro-cellulose or tetranitro-cellulose, the former when the acids have been too strong, and the latter when they have been too weak. It can, however, be prepared in a very pure state by dissolving ordinary collodion wool (rich in tetranitro-cellulose) in warm nitric acid, and precipitating the clear solution by an excess of sulphuric acid, the mixture being kept cool by surrounding the vessel with ice. The collodion wool is introduced into nitric acid of sp. gr. 1·40, and at a temperature of 40-60° C., until the solution begins to assume a strong yellow tinge (which ensues after warming for about an hour). The cloudy solution, after being cooled awhile in the air, is surrounded by ice (to prevent the liberation of red fumes) and filtered through asbestos. It is then re-cooled

with ice and treated with a fourfold volume of concentrated sulphuric acid (sp. gr. 1·840), which also has been cooled with ice beforehand.

After the pentanitro-cellulose has been thrown down, the liquid is poured into a large quantity of water, and the collodion wool is recovered by filtration and washing with water. Further purification is effected by dissolving it in ether-alcohol and re-precipitation with water.

3. Tetranitro-cellulose is formed by treating cotton with a mixture of the concentrated acids—*e.g.*, one volume of sulphuric acid of sp. gr. 1·845, and one of nitric acid (sp. gr. 1·38)—at 65° C. for five to ten minutes. Even when the cotton is treated for fifteen minutes at 80° C. with a mixture of equal volumes of sulphuric acid of the above strength and nitric acid of sp. gr. 1·40, the same product is obtained. In this latter case the product is that known as Schering's collodion wool.

4. Trinitro-cellulose, or rather a mixture of tri- and tetranitro-cellulose in which the former preponderates, is obtained when cotton is treated for five to ten minutes at 65-70° C. with a mixture of four volumes of nitric acid, of sp. gr. 1·38-1·39, and five volumes of sulphuric acid of sp. gr. 1·845.

5. Dinitro-cellulose is obtained by the action of hot, very dilute nitro-sulphuric acid on cellulose, as well as by acting on ordinary collodion wool (tetranitro-cellulose) with potash or ammonia. In the latter case 2-4 grms. of collodion wool are dissolved in 100 c.c. of a mixture of ether and alcohol, alcoholic caustic potash being added in excess and shaken up. The collodion becomes very fluid and yellow-brown in colour. At the end of one to two hours the solution is diluted with a large volume of water, and the free alkali neutralised by an addition of dilute sulphuric acid. Thereupon the dinitro-cellulose collects on the surface of the liquid as a white, flocculent aggregation, which is then filtered, washed and dried, forming a yellowish gummy mass.

A variety of products are also obtainable by the action of nitric acid on cellulose; and these differ from gun-cotton and collodion wool, as well as from each other. In fact even the products known as collodion wool are dissimilar, four varieties being known. Both gun-cotton and collodion-pyroxylin are used in the manufacture of celluloid; and it will therefore be necessary to consider the nature of this pyroxylin as well.

GUN-COTTON.

The discovery of gun-cotton by Schönbein and Böttger, simultaneously, in 1845, excited general interest, it being regarded as certain that gun-cotton was destined to entirely supersede gun-powder in time—a supposition that has only recently been fulfilled to any extent. In industries like celluloid manufacture, where gun-cotton is used, it is made on the spot, owing to the difficulties attended on its conveyance from place to place (though there is little danger when it is transported in a wet state).

Out of the numerous methods of preparing this important raw material we will confine ourselves to two, the two mostly used at present, namely, those of Lenk and Abel respectively.

In all methods it is of great importance that the nitric acid should be pure (free from chlorine especially) and as strong as possible. The cotton, too, should be thoroughly purified, and the finished gun-cotton freed from acid by treating it with water for several days (this operation formerly took weeks). The slightest trace of residual acid imparts to the gun-cotton a tendency to gradual decomposition, and under certain conditions to easily explode.

1. *The Lenk Method.*—The cotton is first boiled for two to three minutes in a solution of potash to free it from fatty bodies, and is then drained in a hydro-extractor, washed with water, drained afresh and dried. It is next placed in a mixture of one part of nitric acid (sp. gr. 1·48-1·49) and three of sulphuric acid (sp. gr.

1·835), which will convert the cotton into explosive gun-cotton in a few minutes.

The cotton after being taken out and allowed to drain is covered up in stoneware pans for a couple of days to complete the conversion of the cotton into pure gun-cotton (hexanitro-cellulose) as far as possible. It is then drained in hydro-extractors, washed with a large volume of water, and laid in running water for three to six weeks. In order to eliminate the final traces of acid, the gun-cotton is boiled with potash solution, followed by draining in the hydro-extractor and washing as before.

2. *The Abel Method.*—In this process cotton-waste (instead of cotton) is nitrated, the material being freed from fat as in the Lenk method, and treated in an acid mixture of identical composition, in which, however, it is left for twenty-four hours instead of a few minutes. The product is drained in the hydro-extractor, washed quickly in plenty of water and re-drained in the extractor, these operations being several times repeated. The gun-cotton is then passed through a machine similar to that used in breaking down paper stock and treated in a "poaching machine" containing a large quantity of warm water. Owing to the fine state of division obtained by the previous treatment, and to the use of warm water and the poaching machine, the gun-cotton made by the Abel process is completely freed from acid in about two to three days, whereas six to eight weeks are required in the Lenk method.

The resulting loose gun-cotton can be compressed into cylindrical form, but the compressed article is not used in making cellulose.

Properties of Gun-cotton.—Judged merely by appearance, there is no difference between ordinary cotton and gun-cotton, or between ordinary paper and paper that has been treated with the acid mixture, the entire structure in both cases remaining unchanged. The gun-cotton is only a little whiter than the other. If, however, gun-cotton be rubbed, especially at a moderately warm temperature, its fibres become strongly electrified and will adhere to the hand. It also feels somewhat harsher than ordinary cotton, and gives out a slight crackling sound when compressed.

Gun-cotton is exploded by a blow or pressure, but the explosion is restricted to the portion actually affected by the shock, leaving the rest undecomposed. A 56-lb. weight can be dropped on gun-cotton from a height of 40 inches without producing an explosion. The cotton is compressed to about one-third its original dimensions by the blow, and it is only when the weight is dropped from a height of 6 feet that a slight detonation occurs, the bulk of the mass being scattered about by the force generated. Even when the weight is dropped from a height of nearly 40 feet the whole of the gun-cotton will not be exploded, but only a small portion, the rest being dispersed to a considerable distance.

When gun-cotton is gradually heated it begins to decompose at 60° C. with liberation of acid fumes, but, as a rule, no explosion occurs below 130° C. If heated more rapidly it will generally detonate at 150-180° C., often even at 136° C., but rarely below 100° C., though cases have been known where gun-cotton has exploded at 70-100° C. whilst being dried on warm, metal supports. Indeed, in exceptional instances, air at a temperature of 25-30° C. has produced an explosion. Hence great care is necessary with gun-cotton, especially in the drying process. Many of the explosions occurring at such remarkably low temperatures may have been due to the imperfect elimination of acid; but thanks to the excellent purifying processes of Lenk and Abel, they are now rare.

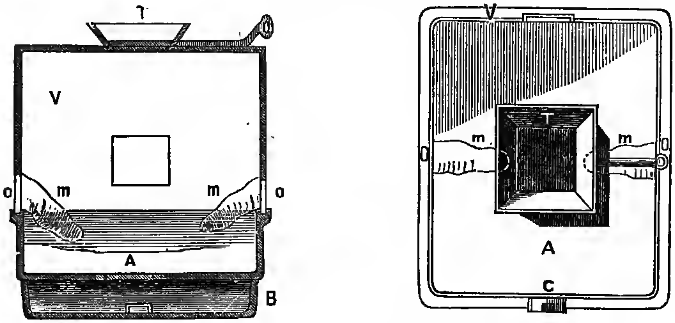
Wet gun-cotton is much safer to handle than the dry material; and indeed when it contains a sufficient amount of moisture it can hardly be considered at all dangerous.

Gun-cotton is insoluble in water, alcohol, ether, chloroform and acetic acid, dilute acids and alkalis; but is soluble in acetone and wood spirit (methyl alcohol).

If saturated with ether, alcohol, carbon disulphide or benzol, gun-cotton decomposes on ignition of the liquid, but without explosion, and a smell of nitrous acid is given off. Wet gun-cotton is readily ignited by burning dry, compressed gun-cotton. It is soluble in a mixture of drying vegetable oil with half its weight of camphor at about 150° C., to form a plastic mass, xylonite, which can be easily moulded, and furnishes, when dry, a yellowish, semi-translucent mass.

SPECIAL GUN-COTTONS FOR CELLULOID MANUFACTURE.

1. According to the method of B. Tribouillet and L. A. de Besancéle, of Paris, the raw materials (paper, cotton, linen, hemp or white woods) are dried at 100° C., ground and then nitrated. This last operation is performed in glass, earthenware or glazed iron vessels, A (Figs. 1 and 2), 7-8 inches deep and mounted on a bottom cooling jacket, B, traversed by a flow of water. Each vessel is surmounted by a glass cover, V, to protect the operator from the fumes. The small hopper, T, in the cover can be closed by a slide, and the lateral opening, C, by a flap.



FIGS. 1 and 2.—Apparatus for making Gun-cotton.

The ground dry materials are treated in this vessel with an acid mixture from a previous operation in another vessel. In order to mix the charge, the operator inserts his arms through the opposite openings, *o*, and the attached rubber sleeves, *m*, which cover the arm down to the wrist.

When the mass has been kept stirred for ten to fifteen minutes with a kind of trowel, it is removed to a press of glazed cast-iron (Fig. 3), with perforated sides and bottom, and is there pressed by forcing down the plunger, P.

The resulting cake is next transferred to a second mixing vessel, where it is treated in a suitable manner with a mixture of three parts of sulphuric acid (sp. gr. 1·834) and two parts of concentrated nitric acid containing nitrous acid in solution, and is afterwards pressed as before. The acid draining from the press is returned to the first mixing vessel, where it is used with a fresh batch of cellulose, after being strengthened with concentrated sulphuric acid or dry sodium sulphate.

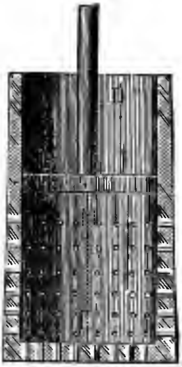


FIG. 3.—Press for Nitro-cellulose.

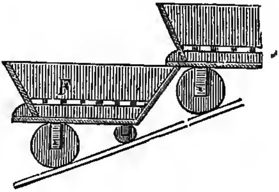


FIG. 4.—Trucks for Washing Nitro-cellulose.

The pressed nitro-cellulose is next stirred up with water and placed in wooden trucks fitted with false bottoms (Fig. 4). These trucks are mounted on wheels of unequal size, so that they can be gradually moved up an incline whilst the washing water runs down out of one into another. The rest of the acid is washed out with water containing a little soda or ammonia, and finally with clean water.

2. According to Hyatt, of New York, it is inadvisable to treat paper in whole rolls or sheets, since in such case the acid will not soak right through; and moreover the manipulation of large sheets of paper entails the use of large quantities of acid. He recommends that the paper be torn into fragments as small as possible, and in this condition brought into contact with the acid. The action of the latter is then more complete and quicker, and a comparatively small vessel can be used.

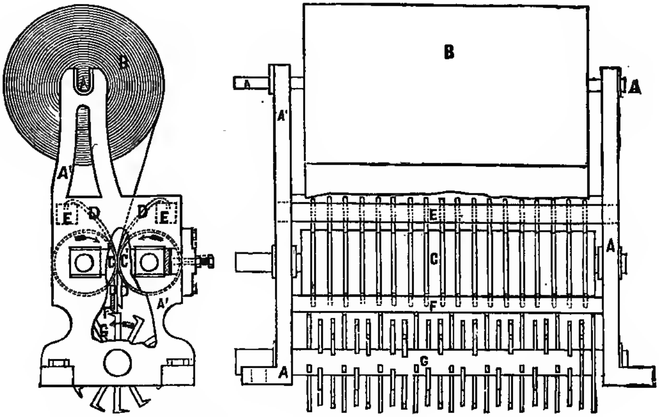


FIG. 5.—Side View. FIG. 6.—Front View.
Hyatt's Paper Tearer for Cellulose Making.

Thin satin paper is employed, and this is torn into small fragments by the apparatus shown as a side view in Fig. 5 and in front view in Fig. 6. This device consists of one or more rotary rollers, A, on which the paper, B, is wound, the rollers being supported by the bearings, A. Only one roller is shown in the drawings.

From this roller the paper passes to the guide rollers, C, one of which is rotated by friction with the other. Each of these rollers is provided with a number of circular channels in which rest the guide wires, D, the upper ends of these latter being bent back and fastened to the bars, E. They extend below the guide rollers, and the one set is attached to knife blades, the cutting edges of which come in contact with the teeth of the rotary breaker, G, so that the paper fed by the rollers, C, is torn into very small scraps.

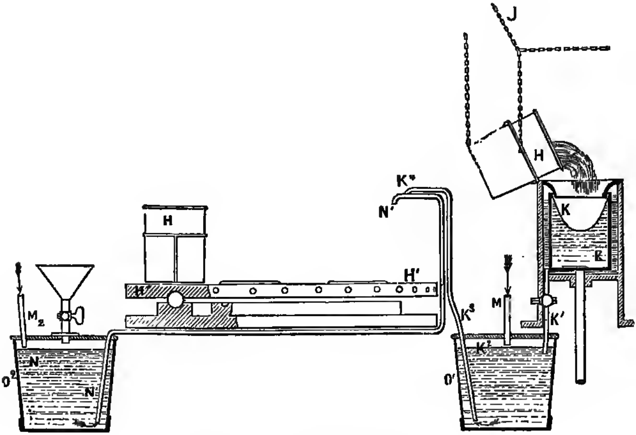


Fig. 7.—Nitrating Vessels.

The rollers are mounted in elastic bearings, so that they are always pressed together whether one or more layers of paper be passing through. The paper can be fed to the machine in sheets instead of in rolls.

The fragments of paper are next placed in the vessel, H (Fig. 7), which contains a mixture of sulphuric and nitric acids warmed to about 26-32° C. The vessel is provided with a vertical stirrer, I (Fig. 8), which can be rotated rapidly and also lifted up out of the acid and lowered into the same.

This stirrer brings the acid and paper into intimate contact, so that the transformation into nitro-cellulose is quickly effected, which done, the stirrer is removed, and the mass is left at rest for about twenty minutes to complete the operation.

The vessel, H, is preferably mounted on a turntable, H′, by means of which it can be brought into position under the crane, J (Fig. 7), which lifts the vessel and discharges its contents into the hydro-extractor, K. In this latter all the excess of acid is expelled from the mass, and runs away through the pipe, K′, into the acid tank, O′, whence it is returned to the vessel, H, which at the same time is charged with fresh acid from the tank, O^2.

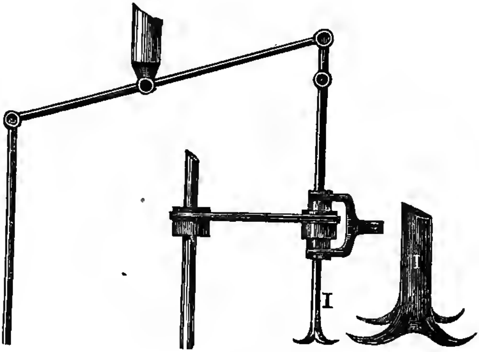


Fig. 8.—Stirrer for Mixing Acid.

The tanks, O′, O^2, are provided with airtight covers, K^2 and N, and the acid is raised through the pipes, K^3 and N′, into the vessel, H, by compressed air, admitted through the pipes, M′ and M^2.

3. *Methods of the Stains Celluloid Co.*—At this company's works, near Paris, the nitro-cellulose is made by submerging paper, made of cotton and linen and weighing about 1¾ oz. per square yard, for some considerable time in concentrated nitric acid, containing a small pro-

portion of concentrated sulphuric acid, the product being afterwards laid in water.

NITRATING CENTRIFUGALISERS.

These machines, which are mainly intended to expel from the interstices of the cotton the air which hinders nitration, are made in different patterns, but have not found general employment in the celluloid industry. This is due to the fact that constant exposure of the mechanism to acids and acid fumes results in injury to the former and an expensive outlay in repairs. In addition a large capital outlay is required to provide a sufficient number of machines to enable the cotton to be left for one to two hours in the extractors. The most widely used machine of this class is that of Selmar and Lange, consisting of a

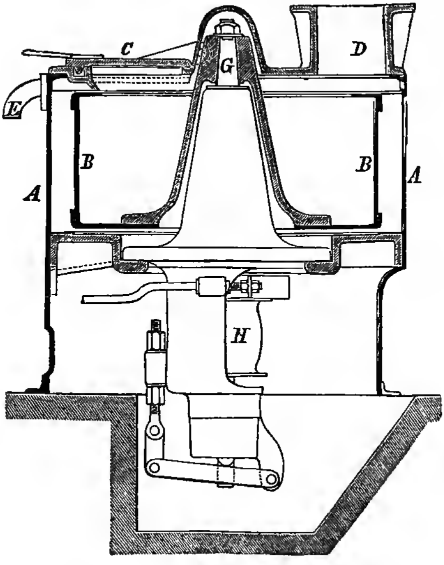


FIG. 9.—Nitrating Centrifugaliser.

hydro-extractor of the ordinary type, fitted with a perforated iron cage, B, 33 inches in diameter, inside the casing, A. The lid is fitted with a hinged cover, C, for the introduction of the cotton. It is also provided with an 8-inch exhaust pipe for carrying off the acid fumes, which are drawn of, in the ordinary manner, by means of a fan, and delivered through earthenware pipes to an absorption tower. The cage is suspended, in the usual manner, by means of a collar-bearing, G, and is revolved by a belt pulley, H, mounted on the lower extension of the central shaft. A band brake, I, brings the machine quickly to a standstill when the process is ended. To work the machine, the acid draw-off tap in the bottom of the casing is closed, and the acid is run in until the vessel is filled to within about an inch of the top. The machine is set running at low speed, and about 17 lb. of cotton is entered by degrees, which raises the level of the acid to within half an inch of the top. The machine is then left to itself, with the lid open, there being no objection to this as the exhaust fan prevents any escape of acid fumes.

In about twenty minutes the operation is completed, the acid is drawn off, the lid closed, and the machine set to run at high speed, which done, the cotton is taken out with a tongs. The advantage of nitrating with this apparatus is that the expelled acid can be easily collected and used over again. The apparatus also enables large quantities to be treated at a time.

COLLODION WOOL.

This substance differs from gun-cotton by being almost inexplosive and by its solubility in a mixture of alcohol and ether, in which gun-cotton is insoluble. The method of preparation also differs, inasmuch as a highly concentrated nitric acid and a low temperature are employed for gun-cotton, whereas in the preparation of collodion wool a rather more dilute nitric acid is used, or this acid is replaced by a mixture of nitric and hydrochloric acids. Frequently also a high temperature (50-70° C.) is used, a weak acid and a warm acid bath favouring the production of collodion pyroxylin.

The collodion wool more particularly used for photographic purposes and the manufacture of celluloid, etc., mainly consists of tetranitro-cellulose, mixed with trinitro-cellulose. Owing to the conditions of formation of pentanitro-cellulose and dinitro-cellulose, these substances, which also are collodion wools soluble in ether-alcohol, are not formed to any extent, if at all, in the preparation of true collodion wool.

METHODS OF PREPARING COLLODION WOOL.

1. One part, by weight, of cotton is immersed in a mixture of 20 parts of sulphuric acid and 9 of powdered saltpetre, in which it is left until a small sample, after a quick washing with water, squeezing, suffusing with alcohol and squeezing again, is found to dissolve rapidly and completely in a mixture of 2 parts of ether and 1 of alcohol. When this is the case the collodion wool is washed thoroughly with water, pressed between linen, and left for twenty-four hours in contact with alcohol, which dissolves out a small proportion and acquires a yellow tinge. The collodion wool is next pressed again and immediately dissolved in 2 parts of 90 per cent. alcohol and 10-20 parts of ether (sp. gr. 0·73).

2. Pure cotton, freed from fat by boiling with a solution of sodium or potassium carbonate, is placed in a mixture of 7 parts of nitric acid (sp. gr. 1·43) and 9 of pure sulphuric acid, at a temperature of 54-58° C. for five to eight minutes, after which it is squeezed and washed.

3. One part of cotton is left for twelve to twenty-four hours at ordinary temperature in a mixture of 7 parts of nitric acid (sp. gr. 1·42) and 9 of sulphuric acid (sp. gr. 1·833), or 8 parts of nitric acid (sp. gr. 1·39) and

20 of sulphuric acid. The collodion wool thus produced is then squeezed and washed.

4. One to 1½ parts of cotton are immersed in a mixture of 20 parts of nitric acid and 30 of sulphuric acid, cooled to 50° C., left therein for twenty-four hours and then washed.

5. To prepare collodion wool from pure satin paper, the latter is steeped in a mixture of 275 parts of nitric acid (sp. gr. 1·47), 275 parts of sulphuric acid (sp. gr. 1·84) and 75 of water. An alternative mixture is one of 50 parts of the same nitric acid, 100 of nitric acid (sp. gr. 1·36), and 100 of sulphuric acid (sp. gr. 1·84). Eighteen parts of the paper are left in the solution for an hour at 55° C., during which process it increases about 40 per cent. in weight. It is then washed with water.

6. Schering's collodion wool chiefly consists of tetranitrocellulose. It has already been mentioned that a collodion wool of analogous composition can be obtained by treating cotton for fifteen minutes at 80° C. with a mixture of equal parts of nitric acid (sp. gr. 1·40) and sulphuric acid (sp. gr. 1·845).

7. Celloidin wool is the purest collodion wool, free from all organic impurities capable of entering into combination with nitric acid, such, for instance, as dextrin, xyloidin, nitro-mannitol, etc.

Celloidin is prepared by dissolving collodion wool in ether-alcohol, precipitating it with water, drying, redissolving and then filtering through a special filtering apparatus. The solution is precipitated again, and the precipitate redissolved in a mixture of ether and alcohol and filtered as before.

The clear filtered collodion is freed from ether and alcohol by distillation to such an extent that the highly viscous residual mass can be poured into moulds while still warm. The gelatinous, glue-like mass obtained on cooling is cut up into lumps, each of which contains a definite weight of dry, pure collodion.

This celloidin is neither inflammable nor explosive.

On ignition it burns like paper, without exploding; heated in a test tube it slowly carbonises. It is used for photographic purposes almost exclusively.

MOWBRAY'S METHOD OF PREPARING NITRO-CELLULOSE OR PYROXYLIN.

The conversion of the raw material into nitro-cellulose is generally attended with numerous manipulations, requiring the constant care of a large number of skilled workmen, and thus entailing very high cost of production. For this reason it is highly advantageous to meet with a process by means of which, with a smaller staff and less supervision, a far cheaper and superior product, ready for further use, can be continuously obtained from a roll of cellulose paper. The principal new features of this process consist:—

1. In passing the unsized cellulose paper through a warm calender, and feeding it direct into and through an acid bath.

2. In feeding a continuous band of cellulose paper into an acid bath at the same time as the immersed and nitrated portion is being withdrawn.

3. In pressing the nitrated paper after leaving the bath, feeding this pressed, nitrated continuous band through a washing liquid and a drying apparatus, distributing a solvent on the moving band, and rolling the latter up.

The various parts of the apparatus are shown in section in Figs. 10-12, whilst Fig. 13 gives a view of the whole, and Fig. 14 represents a modification of the device for applying the solvent.

The frame, 10, which supports both the shaft, 4, and the roll of paper, 7, is fitted with a number of superimposed hollow drying cylinders, which are warmed by suitable means. Between the frame, 10, and the pressure rollers, 8 and 13, is a tank containing the suitably compounded bath of nitric and sulphuric acids for converting the continuous bands of cellulose into nitro-cellulose or pyroxylin. The acid tank contains a pipe, 15, connected with

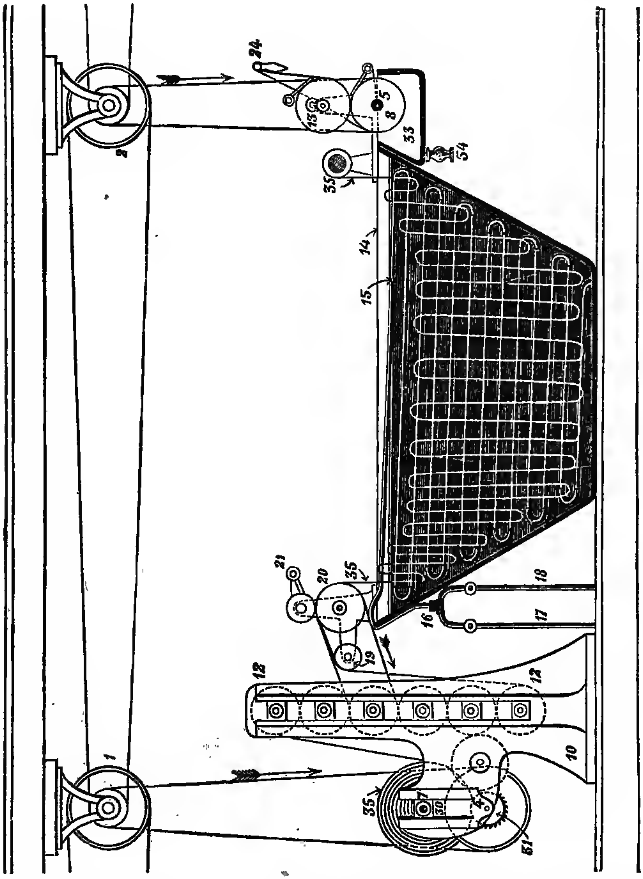


FIG. 10.—Mowbray's Nitro-cellulose Apparatus.

a steam pipe, 17, and a water pipe, 18, by means of a T-piece, 16, for the purpose of enabling the temperature of the bath to be adjusted when necessary. A feed roller, 19, and carrier roller, 20, with a wiper, 21, are mounted near the pressure rollers at the feed end of the

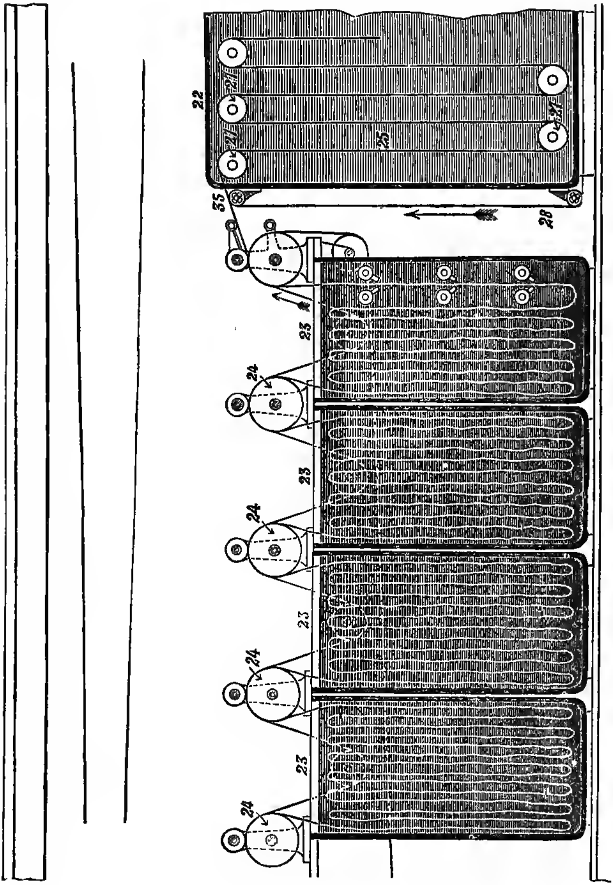


FIG. 11.—Mowbray's Nitro-cellulose Apparatus.

tank. Between the pressure rollers and the drying chamber, 22, are a number of superimposed washing tanks, 23, filled with water, and each fitted with a carrier roller, 24. The latter are rotated in the proper direction by a suitable device driven from the shaft, 5, of the pressure roller, or in any other suitable way. These carrier rollers are preferably covered with an acid-proof coating, or shod with rubber.

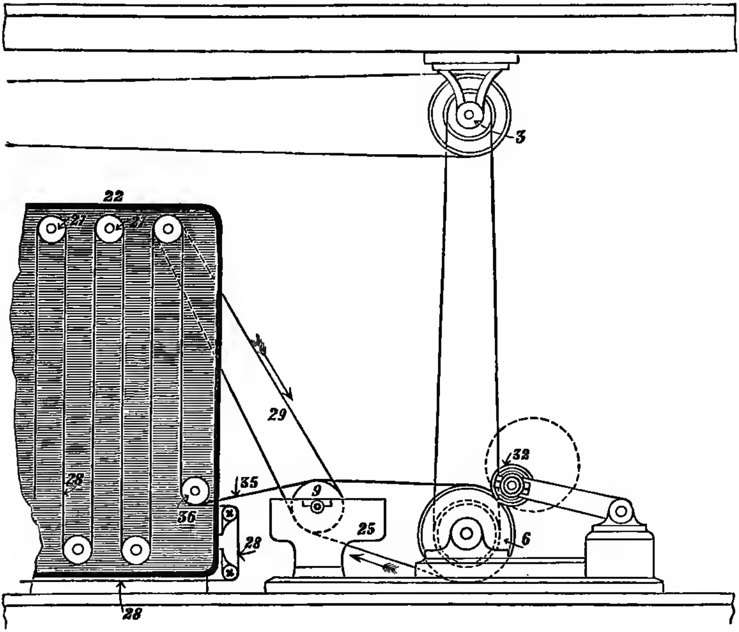


FIG. 12.—Mowbray's Nitro-cellulose Apparatus.

Between the drying chamber, 22, and the roller, 6, is a vat, 25, containing a solvent liquid, which is applied to or distributed on the moving bands by means of the rotary smooth or channelled distributing cylinder, 9.

The solvent liquid may consist of camphor dissolved in water (?), or of water charged with carbonic acid gas;

but no mention is made of any special solvent or of the means for rewinding the paper bands, since various means for these purposes are available.

If desired, suitable dyes may be mixed with the solution, either by dissolving them therein, or adding them ready dissolved.

Passing over the rollers, 27, mounted at the top and bottom of the drying chamber, is an endless belt, 28, by means of which the band of paper is carried through the drying chamber. This belt, 28, is kept in constant motion in any suitable way, such as a belt, 29, driving one of the rollers from the intermediate pulley, 9, which in turn is driven from the shaft, 6, by a belt or other means.

The shaft, 7, is mounted in bearings that slide up and down in vertical slits on the frame, 10, immediately above the driving shaft, 4.

The cylinder, 31, mounted in this manner, carries a perforating device of needle points or the like for the purpose of perforating the cellulose paper on its way through the acid bath, so as to increase the surface and facilitate the penetration of the acid. The winding cylinder, 32, mounted at the end of the machine, for rolling up the band of paper, may be hollow, and mounted in such a manner as to receive motion from the roller, 6, by friction. The pressure rollers, 8 and 13, are situated above a tank, 33, which collects the acid expressed by these rollers, which acid is then returned through pipes, 34, to the acid tank.

The shafts, 5 and 6, are driven by belting from the driving pulleys of the overhead shafting, 1, 2 and 3.

The unsized cellulose paper rolled on the hollow shaft, 7, is drawn upward by the rotary perforator, 31, which penetrates through one or more layers of the fine paper. The latter passes to the topmost drying cylinder, 12, and thence downward between the others in succession until the bottom one is reached, from whence it goes over the rollers, 19 and 20, and under the wiper, 21, to the acid tank, 14,

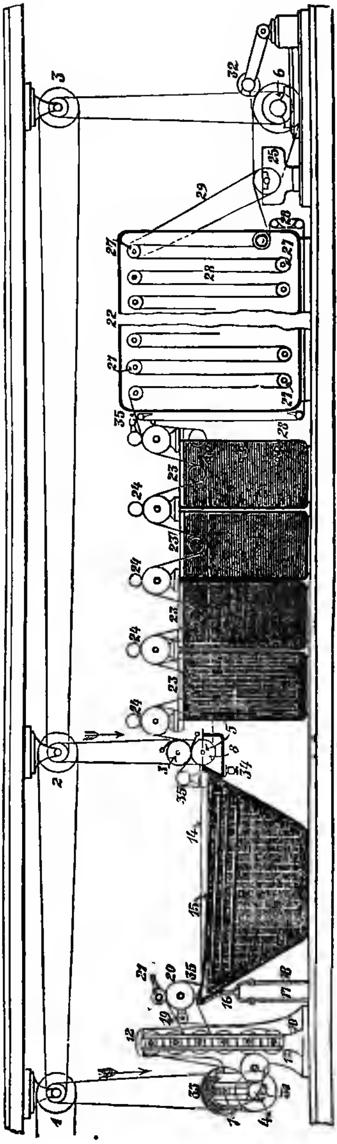


FIG. 13.—Mowbray's Nitro-cellulose Apparatus.

In starting the apparatus, two men—one on either side of the tank—guide the paper from the rollers, 19 and 20, to the farther end of the tank, passing the paper up and down in the positions indicated by the lines in the drawing, this being necessary to prevent the paper from getting entangled. The paper remains ten to twenty minutes in the acid bath, for nitration, and then, while the next following length of paper is being immersed, the portion already in the bath is withdrawn. This operation takes nearly as long as the immersion. On issuing from the acid bath the nitrated paper passes over a guide roller to the pressure rollers, 8 and 13, which squeeze out the superfluous acid, which, as already mentioned, is collected in the tank, 33, and is run off through a pipe, 34, to the acid tank or an empty tank.

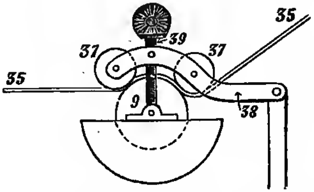


FIG. 14.—Mowbray's Nitro-cellulose Apparatus.

The nitrated paper is next passed over the first roller, 24, through the first water tank, 23, and so on, the superfluous water being removed by the wiper. On leaving the last water tank the paper is fed to the endless belt, 28, which conveys it round the rollers, 27, through the drying chamber, 22.

To hasten the drying process the nitrated paper, before entering the well-ventilated drying chamber, is brought into contact with an absorbent mass that takes up the liquid remaining on the surface.

The endless belt, which leaves the paper band at the rollers, 36, passes back, outside the drying chamber, to its starting-point, to resume its functions until the entire roll of paper has run off. The washed nitrated paper passes over the cylinder, 9, that dips into the solution bath and transfers a suitable amount of the solution to the paper by means of its smooth or channelled surface. This done, and after the nitrated paper has been thoroughly permeated by the solution, it is wound on the hollow cylinder, 32. Instead of using a distributing cylinder, the nitrated paper may be passed through a tank in which it is thoroughly steeped with solution. The rate at which the paper is moved is under the control of the overseer, who can regulate the speed of the motor or the driving shafts by suitable means, and thus increase or lessen the time the paper is left in the acid bath. Two rollers, 37, one in front and the other behind the distributing cylinder, are mounted on arms, 38, which can be raised or lowered by means of screws, 39. By this means the rollers, 37, are adjusted with reference to the surface of the cylinder, 9, thus pressing the nitrated paper with more or less force against the cylinder.

CAMPHOR.

Formerly the term "camphor" was a generic name for crystalline deposits separating out of ethereal oils, or for certain volatile bodies recovered from various vegetable or animal substances; hence the names, Bergamot camphor, Tonka camphor, cantharides camphor, etc. At present, however, the name is restricted to a well-defined series of solid ethereal oils, which are distinguished by a peculiar smell and by other characteristic properties. Chief among these are ordinary camphor and Borneo camphor, in addition to which blumea camphor, rosemary-oil camphor, matricaria camphor, lavender-oil camphor, patchouli camphor, and menthene camphor are also known. These latter varieties exhibit in part the same chemical composition and same chemical properties as ordinary camphor, but differ therefrom physically.

Of late, artificial camphor has been prepared by roundabout, synthetical processes.

JAPANESE (FORMOSA) CAMPHOR, ORDINARY CAMPHOR.

This camphor is furnished by the bark and wood, and to a smaller extent, by the flowers and leaves, of *Laurus camphora*, a large tree of the Laurineæ family, indigenous in China and Japan, where it forms whole woods in some places. On splitting the wood the camphor is found to some extent pure as "tears" or "crystals"; and as much as 22 lb. is said to have been obtained from one tree. The camphor tree, which thrives best in a mild, damp atmosphere, is widely distributed throughout Japan, and occurs in all three of the chief islands, Nippon, Kinhin and Sikok. It thrives best, however, in the south, especially in the provinces of Tòsa and Sikok, where the chief producing centres of camphor are situated.

The recovery of camphor, as practised in Japan and Formosa, is a very primitive process, the wood and branches being chopped small and boiled with water in iron pans, covered over with earthenware pots or hoods filled with rice straw or dry brushwood. Camphor and ethereal oils are liberated with the steam, and the camphor condenses on the rice straw or twigs in the form of a grey, granular mass. This mass, which is highly impregnated with camphor oil, is separated from the twigs or straw as far as possible, and then left for the bulk of the camphor oil to drain away, and placed on the market as crude camphor.

Dr. A. von Koretz reports on the recovery of camphor as follows. As soon as a spot has been found in the vicinity of a few camphor-trees, the camphor-seekers erect a camp and a furnace for preparing the crude camphor; and when the supply is exhausted, the camp is broken up and a move is made to another site.

The selected camphor-tree is felled, chopped into small, regular chips with a hollow-ground, short-handled chopper, the roots are dug up and chopped small, and the whole is packed into baskets and carried to the furnace. The latter is usually erected on sloping ground, near to running water, and is worked as a wet still.

A small ring of stones, *a*, serving as a hearth (Fig. 15), is surmounted by a shallow iron pan, F, about 25 inches across. This in turn carries a perforated cover, E, which is luted on with clay, and also serves as the bottom of a barrel, B, about 40 inches high and 18 inches in diameter at the top. A square opening, D, is provided near the bottom of the barrel, and is closed by a tight-fitting board. The whole is surrounded with a thick layer of loam, C, held in place by bamboo hoops. The opening at the top is covered with a luted lid, G, containing an aperture closed by a plug, K.

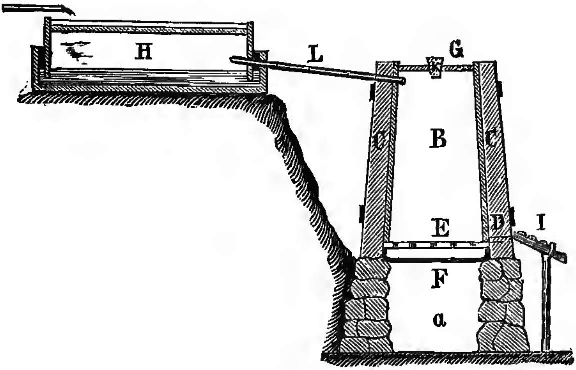


Fig. 15.—Camphor Furnace.

Just under this lid is a bamboo pipe, L, leading to the condenser, H, which is a rectangular box, open below, and divided into five communicating divisions by partitions. This condenser dips into a water tank, and is kept cool by running water over the top.

The lid, G, being removed, the chips are placed in the barrel, B, the lid replaced and luted on with clay, and a certain quantity of water is poured in through the hole, K, on to the chips, whence it trickles down into the pan, F.

Heat is now gradually applied, and the water is boiled gently with a slow fire for about twelve hours; the steam ascending through the chips extracts all the camphor and contained oils, which are deposited on the surface of the water in the condenser, H. At the end of twelve hours the chips are taken out through the opening, D, the apparatus is cleaned, and the camphor collected in H is packed into barrels. A slight pressure applied to the camphor in these barrels suffices to express about 25 per cent. of a water-white oil, a further quantity escaping through the staves when additional pressure is applied. The fairly dry product is generally sent to Osaka, which is the chief storage centre for camphor.

None of the camphor exported has been thoroughly purified, the Japanese article being always freed from the still adhering oil by distillation on arriving in Europe.

There are two kinds of crude camphor, one being the highly esteemed Japanese or Dutch crude, which usually comes on the market in cylindrical form, with plaited straw wrappers, and weighing 1-1¾ cwt. The second kind is the Chinese crude camphor, coming from Formosa *via* Canton and Bombay, and packed in lead-lined boxes containing ½-1¾ cwt.

In Europe, and more particularly in England, Holland, France and Germany, the crude camphor is purified by sublimation, being mixed with a little lime, iron filings or ashes and placed in broad, low, wide-necked, flat-bottomed glass flasks, which are filled about half full and placed on a sand bath. The temperature is rapidly raised to about 120° C., and when all the moisture has been expelled, the heat is very gradually increased to 190-200° C. At this temperature the camphor sublimes, and collects in the top of the flask as a dense, coherent, crystalline mass; camphor oil, which has latterly been used as a substitute for oil of turpentine, being recovered as a by-product.

The refined camphor is in the form of concavo-convex cakes or loaves, with a central hole corresponding to the orifice of the sublimation flask. The weight of the loaves varies between 2 and 11 lb.

American camphor is very dense, and therefore less volatile, owing to having been pressed into cakes, under heavy pressure, after sublimation.

BORNEO CAMPHOR (BORNEOL, SUMATRA CAMPHOR, CAMPHOL, BAROS CAMPHOR).

This product is obtained from *Dryobalanobs camphora*, which is indigenous in Sumatra, Borneo and Java. It collects in cavities in the old stems, but is also said to collect when cavities are made in young ones. The trees die quickly after this operation, and the hollows are then found to be more or less full of Borneo camphor.

This camphor occurs in small, transparent, white pulverulent crystal fragments, which seldom unite to form large lumps. It is white, translucent to transparent, and rather brittle; the smell recalls both camphor and pepper, and the taste is sharp and biting.

Borneo camphor melts at 198° C. and boils at 212° C., both these figures being higher than those of ordinary camphor. It is lighter than water, in which it dissolves with difficulty, but has the same rotatory index as ordinary camphor, is readily soluble in alcohol and ether, and when heated with nitric acid is converted into ordinary Japanese camphor, a property of which use might be made if this variety were put on the European market in larger quantity.

PROPERTIES OF CAMPHOR.

Pure camphor melts at 175° C., but sublimes even at the ordinary temperature, as is shown by the deposition of crystals on the sides of ordinary closed vessels in which camphor is stored. It crystallises in the hexagonal form, and when the crystals are allowed free development, as hexagonal tables. It is readily soluble in concentrated acetic acid, but almost entirely insoluble in water, 1 part of camphor requiring over 1,000 of water for its solution (1,300 parts at 20° C.). The alcoholic solution has a strong dextro-rotatory effect on the plane of polarised light. The crystals exhibit double refraction, but no rotatory polarisation. At 12° C. the sp. gr. is 0·995, but at 6° C. and under, the density is almost exactly that of water, so that camphor crystals scarcely sink at all in very cold water. A more remarkable property of pure camphor is that of spontaneous motion on the surface of water, whereas if contaminated with camphor oil or other impurities it usually no longer exhibits this power. In an unaltered state camphor is pulverisable with difficulty, but becomes pulverulent when moistened with alcohol or other solvents. Pure camphor has an aromatic, rather bitter taste, somewhat heating at first, but afterwards cooling. It is readily inflammable and burns with a smoky flame.

According to reliable reports and certain observations made by Professor Wiesner, no adulterations have yet been detected in camphor.

Camphor possesses the peculiar property of depriving collodion wool and gun-cotton of their tendency to inflammability and explosibility, a fact which is utilised in the manufacture of nitro-glycerine.

Nobel found that a special kind of collodion wool dissolves completely in nitro-glycerine, and furnishes therewith a gelatinous or gummy substance that is much more powerful than kieselguhr dynamite. By the addition of certain substances (acetone, benzol, nitrobenzol) that are soluble in nitro-glycerine, it was found possible to render the new explosive highly insensitive to the chemical impulses that induce explosion, without unduly affecting the power of the explosion itself.

Trauzl pursued the matter further and found that the addition of a very small proportion of camphor (which is exceedingly soluble in nitro-glycerine) furnished an explosive that is highly insensitive to mechanical influences, and especially to shots fired even at a short distance away.

The preservative action of camphor on blasting gelatine is really remarkable. When 10 per cent. of camphor is added the blasting gelatine can no longer be made to explode at all by gradual heating, the mass merely scintillating slowly. When heat is applied rapidly the explosion temperature is too high to be accurately measured with the appliances hitherto available.

This remarkable property of camphor to suppress the ready explosibility of the two most powerful explosives, nitro-glycerine and gun-cotton, is also exercised in the case of celluloid, the explosibility of collodion wool being entirely prevented by dissolving it in camphor. At present, however, the *modus operandi* of the camphor, and the nature of the combination between camphor and collodion, from which celluloid is formed, remains in complete obscurity.

ARTIFICIAL CAMPHOR.

The raw material for the production of artificial camphor is oil of turpentine, or other terpene oils, the process of the Ampère Electro-chemical Co., of Jersey City (N.J.), for example, being based on the action of turpentine on compounds (such as oxalic acid), capable of introducing the CO, OH groups into the molecule of turpentine in such a manner as to form ethereal derivatives that can be converted into camphor by suitable oxidation. Five parts, for instance, of anhydrous turpentine are mixed with one of anhydrous oxalic acid, and the mixture is heated to temperatures below the boiling-point of turpentine, *i.e.*, below 120-130° C. A reaction occurs between the oxalic acid and the turpentine, a mixture of camphor and borneol being formed. These products are separated from any accompanying by-products by the aid of steam, and oxidised with potassium bichromate and sulphuric acid to convert the borneol into camphor, the change being effected by the introduction of one molecule of oxygen and the elimination of one molecule of water. Borneol itself is formed from turpentine and formic acid. According to the Porchester Chemical Co., of New York, artificial camphor is obtained by allowing oil of turpentine (free from ether) to act on oxalic acid at a suitable temperature, the mixture being then treated with lime, the resulting camphor and borneol distilled off and the latter oxidised to camphor. According to Woods (London), terebin monohydrochloride, prepared by acting on American turpentine with hydrochloric acid gas, or by sublimation in a current of steam, is converted into solid camphene by boiling it with sodium acetate and a caustic alkali or carbonate. The camphene is oxidised into camphor by heating with an alkali permanganate, chromate, bichromate, ferrate or chlorate, and very dilute sulphuric acid. Camphor can also be prepared from camphoric acid (obtained from American oil of turpentine) by reduction with nascent hydrogen and boiling with camphene in presence of sodium acetate or formate.

CAMPHOR SUBSTITUTES.

A number of substances have been proposed as substitutes for camphor, by reason of its high price and pungent smell, but up to the present none of them can be regarded as perfect. Among those proposed for this purpose, especially in the manufacture of celluloid, may be mentioned: naphthalene, naphtyl acetate, phenoloxylacetic acid, naphtholoxylacetic acid, with their anhydrides and esters, methylnaphthylketone, dinaphthylketone, methyloxynaphthylketone, dioxynaphthylketone, and derivatives of aromatic sulpho acids of the general formula RSO_2A, in which R represents an acid radicle or a substitution product of the same, and A either an aliphatic (or aromatic) ether radicle, or a singly or doubly substituted amido group. Others are: neutral phthalic acid, alkyl or alphyl esters, esters of the oxamine and oxanil acids, inorganic esters of phenol and naphthol (especially with phosphoric acid, *e.g.*, triphenyl phosphate), halogensubstituted aromatic hydrocarbons, both mono- and polysubstitution products, such as dichlorobenzol, etc., acetyl derivatives of secondary aromatic amines (*e.g.*, acetyl diphenylamine, acetyl phenyltolylamine, etc.), carbonates of phenols, cresols or naphthols, acid or neutral esters of sebacic acid, thio derivatives of the phenol esters (*e.g.*, triphenylthiophosphate), organic esters of sugars (*e.g.*, glucose dibutyrate, lactose, tartaric acid, saccharose acetate etc.), cellulose acetate, nitro products from the distillation of petroleum and mineral oils, acetochlorhydrins, acetines, benzicines, esters of phthalic acid or its anhydride, or esters of succinic acid and aliphatic alcohols, etc., α and β phenynaphthalene, α and β benzylnapthalene, α and β dinaphthyl, α and β dinaphthylmethane, phenol-alcohol esters of phosphoric acid and halogen-substitution products of same, halogen-substitution products of triphenyl, tricresyl and trinaphthyl phosphates, diphenylcresol phosphoranilide, alkyl and alphyl esters of aromatic sulpho-acids, nitronaphthalene, phthalic anhydride, phthalonic acid, benzoltricarbonic acid and esters of these compounds, acetyldiphenylamine, triphenyl phosphate, amylidene dimethyl and diacetyl ether, and formylated albumin.

CHAPTER II.

THE MANUFACTURE OF CELLULOID.

THE fundamental principle underlying the manufacture of celluloid is the property of nitro-celluloses (gun-cotton or collodion wool) of dissolving, under certain conditions, in camphor and forming therewith the new product in question. This solution takes place when nitro-cellulose is warmed, under pressure, with camphor or an alcoholic solution of same, or when brought into contact at the ordinary temperature, with a solution of camphor in ether or wood spirit.

It is easy to understand that the manufacture of celluloid is not without danger, though, given a little care, the risks are not so immense as the opponents of celluloid originally tried to make out.

Among the least dangerous of the methods to be now described should be ranked that in which fused camphor is employed under pressure, since in this case the gun-cotton is kept in a wet state, and therefore almost free from risk, up to the moment when it is changed into celluloid by the camphor and thus loses the power of exploding.

It is open to question, however, whether celluloid is still prepared by this roundabout and lengthy method in Newark, the answer being probably in the negative in view of the far more convenient methods of manufacture by the cold process.

The so-called alcohol process was formerly used in the Stains works, but was attended with the defect that the air-dried and rolled celluloid plates obstinately retained a considerable amount of alcohol, the centres keeping moist even when the plates were quite dry outside.

The most dangerous is the Magnus method, both on account of the risk attending the drying of the cotton, and on the other hand of the volatility of the ether and the risk of an explosion of the ether-laden air in the absence of efficient ventilation and presence of a light.

With the exercise of sufficient care, these dangers can be reduced to a minimum. The method introduced at Stains, using wood spirit, is safe in so far that this spirit begins to boil only at 65° C., and is therefore less likely to liberate explosive vapours at the ordinary temperature than ether which boils at 35° C.

The reactions going on in the formation of celluloid have not yet been identified. It is, however, hardly probable that the camphor and gun-cotton enter into chemical combination, since in observing the behaviour of burning celluloid, by igniting it and blowing out the flame, it is found to glow for a short time longer, strong fumes of camphor being given off at the same time. Apparently, in this case, the propagation of combustion is confined to the gun-cotton or collodion wool, the camphor being heated sufficiently to volatilise but not to ignite. This behaviour during incomplete combustion shows that camphor and gun-cotton exist side by side in celluloid. Hence the formation of celluloid must be classed along with the physical processes analogous to those concerned in the manufacture of leather for instance. The hides of animals when placed in contact with tannin are converted into leather, the tannin being precipitated on the fibres of the skin, which it envelops and prevents them from sticking together in drying. This simple physical process, however, is accompanied by considerable changes in the properties of the animal fibres, the hard, stiff hide, liable to putrefaction, being converted into nonputrefactive, flexible, supple leather. Similarly, it may be imagined that, in the formation of celluloid, the proxylin dissolving in the camphor fills up the minute pores of the latter, and that this physical intimate juxtaposition and fusion of the two substances will probably also result in the fusion of their chemical properties.

MANUFACTURING CELLULOID BY THE AID OF HEAT AND PRESSURE.

1. *Hyatt's Process.*—The process of the brothers Hyatt, of New York, consists in dissolving gun-cotton in molten camphor. The nitro-cellulose for this purpose is prepared by treating satin paper with a mixture of nitric acid (2 parts) and sulphuric acid (5 parts), sprayed on to the paper as it is unwound from a roll. In this stage of the process the greater part of the paper is converted into nitro-cellulose or pyroxylin. It is next immersed in a trough filled with acid, in which it is left for some time, being then removed into a vessel where it is washed with water to remove the superfluous acid. The washed pyroxylin forms a plastic mass, which is collected into lumps, subjected to considerable pressure, dried and broken up again, the lumps being drained in a hydro-extractor, comminuted and mixed with the camphor.

According to other reports the washed and dried nitrocellulose is put through a breaking machine along with water, the latter allowed to drain off, and the mass subjected to very powerful pressure in a perforated vessel to expel the rest of the water and furnish a comparatively solid body, which, however, must retain sufficient moisture to prevent ignition in the subsequent stages of treatment. This mass is mixed with the camphor under water, kneaded, rolled, mixed at the same time with colouring matters and with other substances that are not disclosed by the makers, the object being to impart certain properties, such as transparence, etc., to the product. The usual proportions of the mixture are: 1

part of camphor to 2 of pyroxylin, though other proportions also furnish good results. When mixing is complete the mass is well pressed, to expel any watery constituents still present, and in addition, to bring the particles of camphor and pyroxylin into still more intimate contact to facilitate the solvent action of the former. The dried and pressed mass is transferred to a mould of the desired form, in the upper aperture of which fits a plunger which is forced down on the mass in a hydraulic press. While the mass is still under pressure it is heated by steam to about 130° C., a lower temperature, however, being sufficient for small quantities.

Under this conjoint influence of heat and pressure the solvent action of the camphor is exerted in a high degree, and the formation of celluloid proceeds very rapidly, being completed almost as soon as the maximum temperature has been attained.

On leaving the press the celluloid is hard, but remains elastic, and can be resoftened by warmth or by dipping it in boiling water; and it can be also cut into sheets of varying thickness.

2. *Tribouillet and Besancèle's Process.*—One hundred parts of pyroxylin are intimately mixed with 42-50 parts of camphor, the mixture being wrapped in a very strong cloth, then in a horsehair press-cloth and placed in a warm press. Steam is admitted into the jacket of the press, which latter is also provided with a chamber containing a water spray to condense the vapours of the solvent disengaged in the operation, and enable them to be recovered for use over again. After an hour or more the cakes remaining in the press-cloths are transferred to a heated cylinder press, and thence to a chamber (measuring about 150 cub. ft.) containing calcium chloride or sulphuric acid to absorb moisture, and connected with an air-pump to facilitate the drying process.

MANUFACTURE OF CELLULOID BY DISSOLVING GUN-COTTON IN AN ALCOHOLIC SOLUTION OF CAMPHOR.

A weak alcoholic solution (about 1 part in 8) of camphor is used, this being capable of dissolving pyroxylin when hot, though not at the ordinary temperature.

The gun-cotton is ground to pulp, mixed with the necessary colouring matter, and pressed to expel the watery liquid. The solvent is next added, in the proportion of 1 part to 2 parts of the pyroxylin, and stirred up well, the whole being left in a covered vessel until the solvent has permeated the entire mass. This is a matter of no difficulty, the camphor solution dissolving its way in. Finally the mass attains the same consistency, etc., as that prepared under pressure as already described.

PREPARING CELLULOID BY THE COLD PROCESS.

Preparation with an Ethereal Solution of Camphor. —Fifty parts, by weight, of collodion wool are placed in an earthenware vessel and suffused with a mixture of 100 parts of ether of sp. gr. 0·728 (or 100 parts, by volume, of ether and 5 of alcohol) and 28 of camphor. The vessel is covered with a loaded caoutchouc plate to prevent rapid volatilisation of the ether, which cover is removed at intervals in order that the mixture may be stirred. The greatest care must be exercised in carrying out this process on account of the great inflammability and low boiling-point (35° C.) of the ether, constant and effectual ventilation being essential. In the Magnus works all the windows are kept open in the rooms where the celluloid is being made, in order to prevent any accumulation of ether vapour (which forms an explosive mixture with air). The mixture finally becomes a transparent, sticky, gelatinous mass. The bulk of the ether volatilises during the process, and is not recovered.

The crude celluloid is rolled between a pair of superimposed calendering rollers until it becomes plastic. The rolled, viscid sheets are exposed to the air, and when a certain degree of hardness is attained they are warmed and subjected to powerful pressure. This is done because, up to a certain point, the valuable properties of celluloid are improved in proportion to the pressure applied. The press plates are arranged as follows: first an iron plate, on this a zinc plate, and on the latter the sheet of celluloid to be pressed, this being covered with a zinc plate topped by one of iron. Of course a number of these sets of plates can be placed one above another.

This ether process is only suitable for sheets or rods of moderate thickness, since a thickness of two-fifths of an inch takes ten days to harden.

Magnus used Schering's collodion wool to some extent, and also imported pyroxylin, the latter being—in accordance with the law—carried in a wet, compressed state (minimum water-content, 25 per cent.), and therefore having to be dried before use. So far as is known, the drying process, in the Magnus works, was performed on hot iron plates: this of course necessitating extreme care, and the employment of a temperature not over 60-70° C.

The imported pressed material cannot be dried direct, as in its tangled condition it would greatly retard the solvent action of the ether and camphor. On this account it must, therefore, be pulled apart before drying.

To obtain good celluloid by the ether process it is also highly important that the wool should be dry and perfectly free from acid, otherwise the celluloid is cloudy.

Preparation with a Solution of Camphor and Wood Spirit.—The gun-cotton, after being pulped with water, is treated with a mixture of camphor and wood spirit (methyl alcohol), the principle of the method being identical with that of Magnus. The crude celluloid is also dried in the same way as in the Magnus process.

An essential preliminary to success in carrying out the process is the removal of moisture; and for effecting this purpose J. R. France, of New York, has patented a process, based on the application of hydraulic pressure to removing water, efficiently and cheaply, from large quantities of nitro-cellulose pulp, without risk of explosion.

The extremely sensitive nature of the nitro-celluloses, especially their tendency to explode under pressure when in a dry state, renders the removal of the moisture difficult and dangerous. The method proposed for overcoming these defects is illustrated in Figs. 16-21.

Fig. 16 is a perspective view of the apparatus, but without the cage, which has been removed. Fig. 17 is a vertical section, with the cage shown in position.

Fig. 18 is an enlarged horizontal section along the line 3-3 of Fig. 17, whilst Fig. 18A is a similar section along the line 4-4 of Fig. 17.

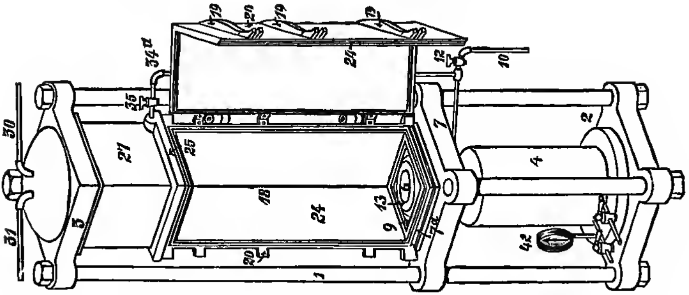


FIG. 16.—France's Drying Apparatus.

The press chamber, of suitable construction, is mounted on the base plate, 2, and terminates at the top in a dome or press plate, 3; 4 is the cylinder and 6 the plunger of the hydraulic press, the plunger passing through the opening, 8, of the lower press plate. This plate carries a plate, 7*a*, fitted with a flange, 13, and a well, 9, forming the connection with the press chamber or cage and fitted with a discharge pipe, 10. The flange, 13, supports the lower edge of the cage or press chamber, 14, which is made up of sections, as shown in Figs. 19-21. The cage can be taken apart at the opposite ends, so as to make the interior accessible. One half of the cage is fitted with a rib, 14*a*, and inward flange, 14*b*, which fits against the inner surface of the cage. Above is a second rib, 14*c*, which can be either detachable or made in one piece with the other half of the cage. Inside is mounted a false bottom, 15, which fits easily, resting on the flange, 14*b*. It is perforated with holes, 16, and provided with channels, 17, round the outside. To facilitate handling, the cage

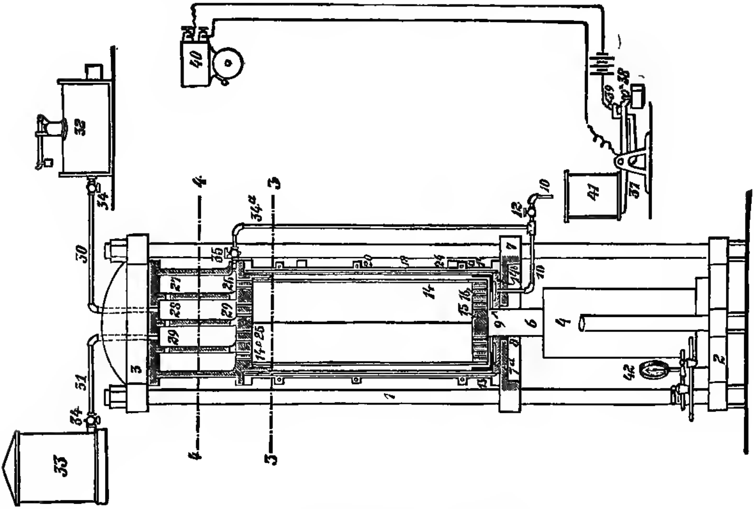


FIG. 17.—France's Drying Apparatus.

is preferably made of wood, lined with zinc. Inside the frame, 1, of the press, and over the plate, 7, is a press chamber, 18, which is divided cornerwise, the two halves being connected together by hinges. When this chamber is closed, the sides surround the flange, 13, of plate, 7*a*. The outside of the chamber is provided with ribs, 19, and sockets, 20, to receive the bolts, 21, for closing the chamber. The bolts carry wing nuts, by means of which the joints can be tightly closed, the said joints being lined with strips of packing material, 23, in the grooves, 24. The press chamber encloses the cage, on which rests the flange, 13, of the plate, 7*a*.

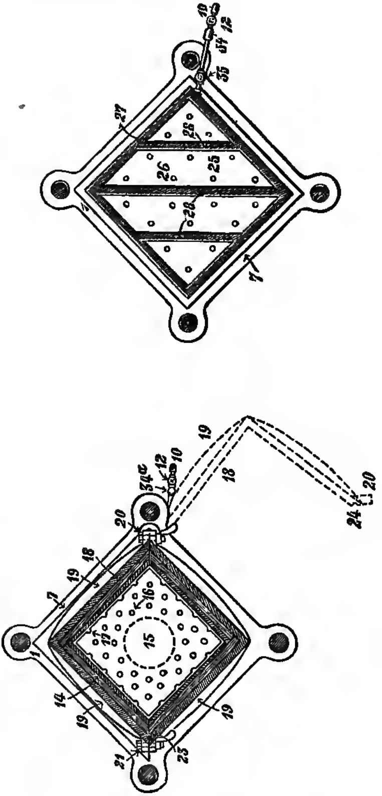
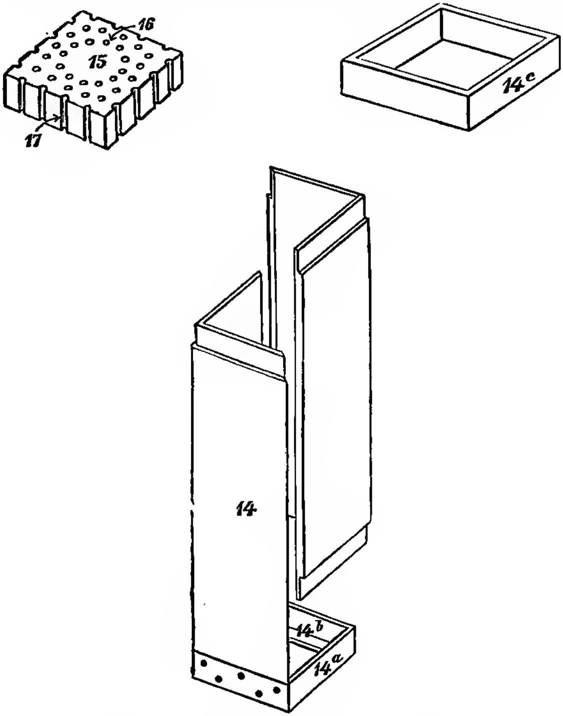


FIG. 18.—France's Drying Apparatus.

At the top of the press is a strong transverse wall, 25, forming the press head. This wall is pierced with holes, 26, extending to an upper chamber, 27, divided by partitions, 28, provided with openings, 29, above and below.

In connection with these two chambers are two pipes, 30 and 31, each provided with a tap, 34, and leading to an air compressor, 32, and an alcohol tank, 33, respectively. A pipe, 34*a*, that can be closed by means of a tap, 35, leads from the bottom of the chamber, 27, to the outlet pipe, 10.



Figs. 19-21.—France's Drying Apparatus.

On a level with the press is arranged a special form of weighing machine, the object of which will be explained later. If necessary, electric contacts, 38 and 39, can be provided on the beam of the machine and connected by wires with the bell, 40.

The apparatus is employed in the following manner. The nitro-cellulose coming from the washing tank is placed in a hydro-extractor which is kept running until the pulp contains about its own weight of water. The mass is then taken out and made up into lumps weighing about 2 lb. each. A piece of muslin having been placed on the false bottom, one of the lumps of nitro-cellulose is laid on it and covered with a second layer of muslin. On this again is laid another lump of nitro-cellulose, and so on until the cage is full. The cage being inserted in the press chamber, the latter is fastened up, and the hydraulic press set in motion, the plunger rising and lifting the false bottom, 15, thus pressing the nitro-cellulose between the latter and the press head, 25. The pressure is raised to about 400 lb. per square inch, and this is maintained for an hour, during which time the expressed water runs down through the holes, 16, and channels, 17, of the false bottom into the well, 9, of the plate, 7*a*, and away through the pipe, 10, whilst the water forced upward through the cross wall, 25, is drawn off through the pipe, 34*a*, to the pipe, 10*a*.

After the pulp has been pressed for about an hour, the tap, 34, is opened to admit air from the compressor, 32, this air penetrating the pulp and driving out most of the residual water therein. The compressed air is admitted for some little time after the water has ceased to flow, and then the tap is turned off and 90 per cent. alcohol is admitted to the chamber, 27, from the alcohol tank, 33, by opening the tap, 31. From this chamber the alcohol trickles down by gravitation through the cross wall, 26, and through the nitro-cellulose pulp, driving in front of it the traces of the heavier liquid, water, still left therein.

Practical experience with this apparatus has shown that about 30 per cent. of the water is expelled from the nitro-cellulose by the pressure employed, and a further 20 per cent. by the use of compressed air afterwards, so that only about half the original quantity of water is left in the mass. This initial weight of water being known, the degree of drying obtained can be easily ascertained by collecting the effluent water in a vessel, 41, placed on a suitably counterpoised balance, 37. When the ringing of the electric bell, 40, indicates that sufficient water has been collected in the vessel, 41, the tap admitting the alcohol is closed and the vessel, 41, is replaced by another to receive the mixture of alcohol, which drains away from the nitro-cellulose and can be distilled for recovering the alcohol. The compressed air tap is turned on again and the alcohol expelled until the nitro-cellulose contains 40-50 per cent. of its own weight of that liquid, whereupon the air supply is stopped, the press plunger is lowered and the press chamber opened. The cage now contains the nitro-cellulose or pyroxylin in compact layers, separated by the sheets of muslin, and therefore easily detachable. The amount of camphor necessary to fully convert the nitro-cellulose or pyroxylin into celluloid is now placed, along with the colouring matters and pigments, between the several layers of material, which are next piled up in zinc-lined chests and covered up tightly, to be stored until they can be rolled in the usual way.

To enable the pressure in the apparatus to be regulated according to requirements, a pressure gauge, 42, is mounted on the hydraulic cylinder.

The apparatus and method possess the following advantages. 1. The rapid expulsion of water from the pyroxylin, thus enabling a large quantity to be dealt with daily at a low cost. 2. Uniform distribution of the solvent, so that all parts are impregnated with alcohol, thus facilitating the further treatment with solvents. 3. Absence of danger in the drying process, the pressure applied to the pulp being low, and the pulp itself remaining moist throughout. The method is rapid, simple, reliable and cheap in operation, and the alcohol remaining in the nitro-cellulose, and afterwards combining with the camphor, can be recovered by distillation.

CHAPTER III.

THE EMPLOYMENT OF PYROXYLIN FOR ARTIFICIAL SILK.

WITHIN a comparatively brief space of time there has arisen an entirely new industry, that of the manufacture of artificial fibrous materials from dissolved nitro-cellulose, which products are destined to provide the textile industry with a new material, artificial silk, that is already largely used.

Hilaire de Chardonnet was the first to take out a patent for making weavable threads from liquids obtained by the use of alcohol, ether, a reducing metallic protochloride, a small quantity of an oxidisable organic base and pyroxylin, the product being drawn out by means of special appliances into fine threads, which were then hardened. To prepare the solution, 100 grms. of pyroxylin, 10-20 grms. of a reducing metallic proto-chloride (ferrous, chromous, manganous or stannous chloride), about 0·2 grm. of an oxidisable organic base (quinine, aniline, rosaniline) were used along with 2-5 litres of a mixture of 40 per cent. ether, 60 per cent. alcohol and dissolved colouring matter, the pyroxylin being dissolved in the greater portion of the alcohol-ether mixture, while the rest was employed to dissolve the metallic protochloride, the organic base and the colouring matter, the two solutions being afterwards united. When the hot liquid prepared in this way is allowed to escape through a fine nozzle surrounded by a cooling liquid, the superficial portion of the thin stream of collodion-like liquid sets immediately, and thereby forms a solid thread. This thread represents an external, solid tube, enclosing an internal fluid column. The threads can be drawn out still finer in the air, and resemble silk in their lustre.

The apparatus originally used by Chardonnet (Figs. 22 and 23) consists principally of organs for spinning the collodion, capillary tubes, *a* (Fig. 22), surrounded by a tube, *k*, filled with water. These organs are arranged, in the patented machine, about a main tube, B (Fig. 22), which is surrounded by two channels, C, provided with a circulation of water. The working orifice of each spinning organ is surrounded by a lightly gripping pair of tongs, *m*, made of two flat springs, and all these tongs receive through bell-crank levers, *o*, and bent arms, *pp*,

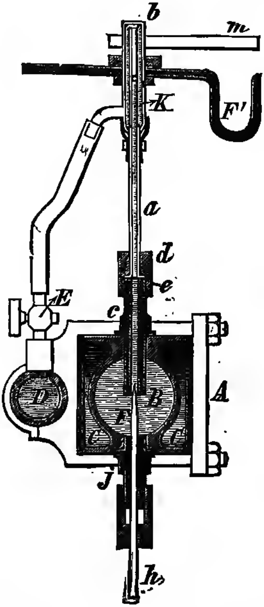


FIG. 22.—Chardonnet's Artificial Silk Apparatus.

a rising and falling swing motion from the spinning organs to the bobbins or reels, in such a manner that newly formed threads, just running over the edge of the spinning organ, or thick breaking threads, stick to the tongs and are conducted to bobbins, whereas the tongs rise and fall empty so long as the threads do not break in spinning. A rotary brush, H, cleans the tongs on reaching the upper limit of motion. The spindles, S, of the bobbins, R, for winding the silk are mounted on loose cheeks, P, of the revolving shaft, O, and carry small rollers, V, which

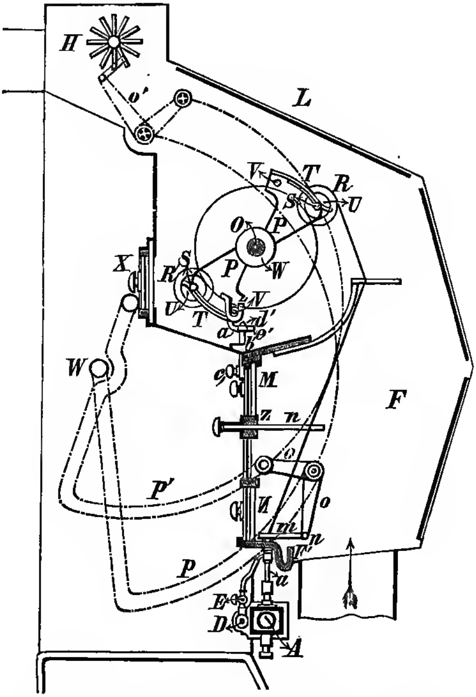


FIG. 23.—Chardonnet's Artificial Silk Apparatus.

make contact with the periphery of cams, Q, mounted on the shaft, with the result that all the bobbins turn simultaneously and the cheeks also are moved simultaneously for the purpose of replacing the full bobbins by empty ones. The machine is enclosed in a casing, traversed by a current of warm air to remove the vapours of ether and alcohol, and convey them, for purposes of recovery, through a series of condensers, the first of which contains a concentrated solution of sodium carbonate, the second and third being charged with concentrated sulphuric acid. The bulk of the alcohol and ether settles down on the sodium carbonate solution, whilst the remainder is absorbed by the sulphuric acid.

Other inventors occupied themselves with the development of Chardonnet's invention, and a few of the methods elaborated may be mentioned here.

Vivier, for instance, dissolves gun-cotton or cellulose in the strongest acetic acid, with the addition of a little gelatine. The cellulose is obtained from the powdered fibres of black poplar or boxwood, nitrated by the usual method.

E. Breuer patented a process for producing coloured threads (or with metallic lustre) from collodion without spinning. A roller, of metal or other solid material, is coated, first with a layer of collodion, then with dissolved glue, then with more collodion, and so on alternately, until a certain desired thickness is obtained. The roller prepared in this way is put in a screw-cutting lathe, and the coating is cut through spirally, furnishing a continuous thread that can be unwound off the roller and reeled.

According to H. de Parville, collodion wool is dissolved in a mixture of ether and alcohol, and the resulting solution is placed in a tinned copper vessel, in which a pressure of several atmospheres is generated by means of an air-pump. In the bottom of this vessel is a sloping surface, in which are mounted a number of vertical glass tubes, terminating in fine nozzles. A second tube surrounds each of the first, and by means of suitable connections enables a slow circulation of water to be maintained round the tubes communicating with the vessel.

Under the influence of the pressure the collodion gradually issues from the capillary openings of the tubes, and solidifies as soon as it comes into contact with water. The threads are seized by an automatic reel and wound on revolving bobbins. After denitration the threads are gelatinous, can be easily impregnated with colouring or saline matters, are no longer explosive, and can be rendered incombustible by passing them through ammonium phosphate.

The method of F. Lehner consists in the use of a mixture of copal or sandarach, linseed oil, nitrated cellulose and a salt that prevents combustion. Three solutions are prepared from these ingredients, and mixed. The first solution consists of 500 parts of finely powdered copal or sandarach in 2,400 parts of ether, the two being shaken up in a tightly closed flask at a medium temperature, left to clear, mixed with 100 parts of linseed oil and filtered. The second solution is prepared by immersing satin paper cellulose, cotton or spinning waste in a solution of ammoniacal copper oxide (10 parts of copper sulphate in 100 parts of ammonia of sp. gr. 0·975) for about fifteen minutes, the proportions being about 1,000 parts of cellulose material to 12,000 parts of solution. This causes the fibres to swell up, and facilitates nitration. The mass taken out of the bath is thoroughly washed in a large volume of warm water, squeezed and well dried. It is then introduced, in a flocculent state, into a mixture of 4 parts of sulphuric acid (sp. gr. 1·84) and 3 of nitric acid (sp. gr. 1·4) warmed to 75° C. and well stirred, the acid being poured off after five minutes. The resulting nitro-cellulose is thoroughly washed with water, dried, suffused with wood spirit (9 parts to 1), shaken up until completely dissolved, and set aside for a week in a cool place to clarify, the clear liquid being poured off from the sediment. Solution three consists of 100 parts of sodium (or ammonium) acetate in 1,000 of dilute spirit of wine, the solution being filtered.

These three solutions are mixed together, so that for each 1,000 parts of nitro-cellulose there are 200 of copal or sandarach, 50 of linseed oil and 100-200 parts of sodium (or ammonium) acetate. This mixture, the basis of the threads, is allowed to escape through a narrow orifice, the solvent being evaporated by warmth and condensed for use over again.

In the apparatus employed the mixture escapes from a reservoir, through a pipe and on to a moving smooth surface, namely, a cylinder slowly revolving on a shaft. To hasten the hardening of the soft threads, the part of the cylinder behind the nozzles is covered with a casing that is kept at a high temperature by means of a steam-pipe. The radiant heat quickly evaporates the solvent in the threads on the cylinder and solidifies them. The motion of the cylinder forces the evaporated solvent into a space where it is condensed by a cooling vessel surrounding the cylinder, and drains away at the bottom. This cooling space is fitted with perforated baffles to guide the vapours into contact with the cooling surface. The hardened threads are continuously removed from the cylinder (which is enclosed at every other part), any broken threads being lifted from the surface of the cylinder by a rotary brush. The cylinder is kept dry by contact with a pad of felt. If the threads issuing from the nozzle be brought into contact with a finished thread of other material, such as cotton or wool, a mixed thread is obtained, which is drawn off in the same way; or the thread can be impregnated with a mixture beforehand and then passed through the machine. Instead of a moving surface, a fixed surface and movable nozzle can be employed in forming the thread.

These older methods and devices have, in the course of a few years, been succeeded by a number of others, relating to either an improvement in the spinning process, accelerating the hardening, washing and denitrating, or impregnating the threads with flame-proofing salts. It would be beyond the scope of the present work to go into these processes more closely, and it will be sufficient to say that both fine threads of artificial silk and coarse threads in imitation of bristles are now produced by this means.

DENITRATING AND COLOURING PYROXYLIN.

Owing to the high inflammability of nitro-cellulose and the explosibility of the higher nitro-compounds, a desire has long existed that the cellulose should be denitrated before putting it through further treatment. Here again Chardonnet, the inventor of artificial silk, was the first to employ a fairly suitable method for this purpose, by treating the pyroxylin in a bath of nitric acid, diluted with water to the sp. gr. 1·32, and maintained at a temperature of 32-35° C. The pyroxylin gradually parts with its nitric acid and in a few hours changes into a lower category than tetranitro-cellulose, *i.e.*, it contains over 6-6½ per cent. of nitrogen.

The desired denitration can be determined by analysis, either by the Schloesing method (liberation of nitric oxide in presence of hydrochloric acid and ferrous chloride), or by a solution test; and the fact that denitration is effected by this process has been demonstrated by numerous analyses. The operation is nearly completed when the substance ceases to be attacked by the usual solvents of collodion wool, *viz.*, ether-alcohol, nitrous ether, etc. The material is then washed with lukewarm water and dried in a current of warm air. The completion of the operation is indicated by the incipient softening of the pyroxylin.

In this reaction the liquid concentrates in proportion to the nitric acid abstracted from the pyroxylin; the same bath can be used over and over again after being restored to the desired concentration. This factor and the temperature of the acid may be varied between wide limits, the length of the reaction varying inversely with the warmth and concentration of the nitric acid.

To colour the pyroxylin, it is washed with lukewarm water on leaving the bath, then dipped in a bath of dye, rewashed in cold water and finally dried in warm air. When the method is applied to artificial silk, it is unnecessary to introduce metallic proto-chlorides and oxidisable organic bases or alkaloids into the solution for the purpose of reducing the explosibility of the spun collodion.

Various reducing organic substances, and even pure water, will denitrate pyroxylin, but in a smaller degree than nitric acid. At temperatures above 15-20° C., pyroxylin and alcohol react quickly enough; hence, in denitrating artificial silk it is preferable to operate in the cold.

Collodion cast into plates and moulded in various ways can be used in place of glass, mica or horn, for windows, vessels, transparent frames, etc.

Cupro-compounds are excellent denitrating agents, and recent experiments have shown that they will act well, not only in acid or ammoniacal solution, but also in the absence of either acid or ammonia and merely in presence of alkali chlorides. Denitrating solutions can be prepared in various ways, such, for instance, as dissolving cuprous chloride in alkali chlorides, or by warming the nitro-cellulose under treatment in a mixture of cuprous chloride and common salt (for instance) in presence of metallic copper. Typical proportions would be: 1 part of nitro-cellulose, 2½-6 parts of cuprous chloride, 20-50 parts of common salt and sufficient water to prevent any crystallisation in the solution. The temperature may be kept at 25-100° C.

Other methods for diminishing the inflammability of celluloid, or making it incapable of ignition, are given below.

The celluloid solvent is treated with an addition of a siliceous ether, such as amyl or methyl silicate, or a suitably dissolved solid siliceous ester like ethyl disilicate.

In the presence of bromates in the mass an addition of ferric chloride dissolved in the cellulose solvent will generate gases that stifle combustion.

An alcoholic solution of calcium chloride, of about 20 per cent. strength, is added to an acetone solution of celluloid (about 10 per cent. strength), in such quantity that 10 parts of celluloid are present to each part of calcium chloride. The solvent is evaporated, and the residue is rolled out in thin sheets and dried at the ordinary temperature. The proportion of calcium chloride can be raised to 15-20 per cent. Calcium chloride may also be added to comminuted pyroxylin, the mixture being then moistened with alcohol and milled at 20° C.

A good product is obtained by mixing solutions of nitro-cellulose compounds with acetyl cellulose. To 25 parts of celluloid solution are added 6 parts of magnesium chloride dissolved in alcohol or denatured spirit and mixed with 3 parts of finely ground asbestos.

To 1,000 parts, by weight, of celluloid are added 1,500 parts of fish oil, 400 of gum-arabic, 100 of gelatine and 40 of colza oil.

Celluloid or nitro-cellulose, dissolved in acetone, is mixed with solutions of aluminium chloride, strontium, magnesium or calcium chloride in methyl alcohol.

Nitro-cellulose is mixed with aluminium salts, in which case camphor may be partly or entirely dispensed with. In another method a saturated solution of aluminium chloride or nitrate in acetyl acetate is mixed with nitro-cellulose.

Stocker's Uninflammable Celluloid.—Stocker prepares a mass possessing the valuable properties of celluloid: transparency, flexibility, toughness and perfect plasticity, associated with that of being combustible with difficulty.

At the moment of formation the finished, but still soft, mass of celluloid is treated with an addition of stannous chloride, which remains in the mass, and, owing to molecular combination, entirely prevents combustibility, provided a sufficient quantity has been used.

One hundred parts, by weight, of nitrated cotton or nitrated paper are mixed with 400 parts of camphor and 70 of stannous chloride, the whole being moistened with 100 parts of alcohol. After standing twelve hours the mass is raised to 60° C. by passing it through warm rollers, and is kneaded until perfectly homogeneous. By increasing the proportion of alcohol, the mass can be kneaded and worked in the cold.

This process furnishes a transparent mass, which can be worked in the usual way. To obtain colours, cuprous chloride is added for green, ferrous chloride for brown and black. The mass will burn only when held directly over a flame, and ceases to burn or even glow immediately it is taken away again. For special articles, such as cartridges, that are desired to be more readily combustible, all that is necessary is to reduce the proportion of stannous chloride and thereby increase the inflammability.

Streubel's Vegetalin.—Dry cellulose at 15° C. is suffused with sulphuric acid (58° C.) and left in contact therewith for some little time, after which the acid is washed out completely with water, the cellulose being then dried and milled. It is next intimately mixed with resin soap in a mortar and treated with a solution of aluminium sulphate. The mixture of modified cellulose and aluminium resinate is dried, and pressed into blocks in a hydraulic press. The blocks are cut into sheets, which in turn are moulded into the desired shape by means of hydraulic pressure.

Celluloid and Cork Composition.—According to the method of Hagemann, ground cork is impregnated with a solution of nitrated cellulose in ether and alcohol, and pressed into moulds, the pressure being maintained until most of the solvent has evaporated and the mass retains its shape when the moulds are opened. For small articles this takes four to six days, and to facilitate evaporation the moulds are perforated and lined with wire gauze. The product known as "Subrit" is used as a substitute for cork, bottle corks, insulating plates, etc.

Koller's Celluloid Substitute.—Highly concentrated collodion, prepared by immersing nitro-cellulose in ether-alcohol, methyl ether, acetic ether, acetone, or mixtures of these, until the solvent is completely saturated, is mixed in an autoclave with a pulpy mass of nitrated cotton or paper that has been steeped with oil of turpentine containing sulphur, castor oil and resin, turpentine resin, shellac, colophony, mastic, Canada balsam or copal resin, in solution. The mixture is carefully heated in an autoclave to 100-150° C., the pressure being raised simultaneously to 12 atmospheres by means of an air-pump. The resulting perfectly transparent, gelatinous mass can be formed, for example, into thin sheets serving to carry a sensitive layer of emulsion for photographic purposes, or can be cut with zigzag edges and pressed into tubes or belts.

Incombustible Celluloid Substitute.—This product is obtained by treating cellulose with strong caustic potash and subsequently introducing vapours of carbon disulphide, the process furnishing a gelatinous, pale yellow transparent mass of high viscosity and adhesive power. The cellulose is eliminated from the mass by washing with salt and water, leaving as the residue a compound of potassium, sulphur and carbon, the elasticity, transparency and solubility varying according to the amount of cellulose removed. This mass is also claimed to be suitable for the preparation of a perfectly transparent paper that is entirely unacted on by water.

Xylonite or Fibrolithoid.—This is a variety of celluloid in a solid or liquid form. The latter is obtained by dissolving 40 parts of nitro-cellulose in 20 parts of cedar wood oil and 40 of amyl acetate, and is used as a dipping lacquer for metals of all kinds; and the solution can be also applied to all kinds of textile fabrics. To obtain solid xylonite the solution is evaporated. Another recipe reads: Nitro-cellulose 10 parts, amyl acetate 30, amyl alcohol 25, cedar wood oil 2, benzine 3.

Xylonite is prepared as follows, according to the patent specification: the dried finely divided pyroxylin compound is treated with a solution of camphor in a solvent that does not dissolve pyroxylin. The solvent is then expelled and the mass is finally exposed to hot alcoholic vapours.

CHAPTER IV.

PROPERTIES OF CELLULOID.

CRUDE celluloid, free from all additions of colouring matter, body colours or other substances designed for the production of special effects, is nearly colourless, and in thin layers is as clear as glass or faintly yellow, very elastic, transparent to translucent, hard, solid, nearly unbreakable, and can be cut with a knife or shears. It can be made harder or softer by suitable additions, though all attempts to render it soft and plastic like guttapercha have failed. Contrary to earlier statements, celluloid is not electrified by friction. Celluloid has a faint smell of camphor, this smell, which is not disagreeable, becoming stronger when the mass is rubbed and forming a means of identifying celluloid. Heated to 125° C. it becomes plastic, and in this state can be moulded into any desired shape. Separate pieces will coalesce on mere contact when warmed. At about 140° C. celluloid suddenly loses its colour and transparency, and at about 5° higher decomposes with liberation of pungent, readily inflammable vapours.

Warm, plastic celluloid forms an excellent cement for metals, a property of considerable utility in the production of inlaid work.

Celluloid softens in warm water, becomes flexible and somewhat plastic, so that it can be easily moulded to any shape. This behaviour, also, is very valuable in the manufacture of celluloid articles, since the moulding process is greatly facilitated, loss of material is prevented and time is saved.

When ignited, celluloid burns with a smoky flame and more rapidly than sealing wax, a smell of camphor being apparent at the same time. When the flame is blown out shortly after ignition, the mass continues to glow briskly and to give off thick fumes of camphor that will soon darken a small room. Undoubtedly the gun-cotton burns in this case at the expense of its own oxygen, but the temperature is not sufficiently high to ignite the distilling camphor. This behaviour indicates most clearly that celluloid is not a chemical combination of camphor and gun-cotton or collodion wool, since it is characteristic of chemical compounds that the substances entering into combination cease to exist independently in the compound.

Celluloid can be ignited only by a naked light, and if heated in a vessel of any kind it simply decomposes, as already mentioned, at about 150° C., suddenly and completely, with the liberation of a good deal of smoke. In no case, however, is there any question of an explosion, for celluloid cannot be exploded either by pressure, shock, percussion, friction, heat or any other means. Celluloid is no longer gun-cotton, but a substance differing therefrom in all its properties.

The property of celluloid of softening in hot water enables it to be cut into sheets of any desired thickness; and attach itself like putty, to wood, marble, etc.

If two surfaces of celluloid be coated with collodion and pressed together, the two sheets, etc., will unite firmly to form a solid whole.

Celluloid is insoluble in water, and on this account is suitable for making domestic articles, such as knife handles. Though it is not directly attacked by concentrated sulphuric acid, it gradually dissolves therein in the cold, a small piece entirely disappearing in about thirty-six hours. It also gradually dissolves in concentrated nitric acid, and in boiling caustic potash.

The tensile strength of celluloid is very considerable. According to the results of a few crude tests, the elastic limit is about 200,000-240,000 lb. per square inch, that of iron being about 130 times as great, and that of wood about seven times as great.

The elasticity is also high, as can be demonstrated by an easy experiment. The tip of a celluloid hairpin, for instance, can be bent round until the two ends meet, and back again until the ends meet at the opposite side; and this can be done any number of times, the pin retaining its original appearance when straightened out. To break off the tip it must be bent to and fro rapidly with considerable force. These simple tests clearly show the extreme elastic pliability of celluloid. The substance can be stained any desired colour, and the colouring matter is not absorbed merely superficially, but permeates the whole mass—as can be seen from the fractured surface of celluloid articles. By means of suitable additions and treatment, celluloid can be made to imitate a large variety of materials, for which purpose it is largely used. In all conditions its surface is extremely smooth and lustrous; it can be sawn, filed and turned in the lathe, and in general treated like horny materials.

Celluloid can be rolled, polished, pressed, cut and hammered, and can also be kneaded at a temperature of 145° C., so that, occasionally, it may take the place of metals, stone, wood and wax.

The specific gravity of celluloid varies according to the degree of pressure it has sustained in the manufacture, the mean being 1·5.

CHAPTER V.

TESTING CELLULOID.

THE qualitative examination of celluloid, that is to say, the actual composition of the ingredients, is (according to Heinzerling) attended with no difficulty, whereas the quantitative determination is far less easy.

Mineral adjuncts can be detected by treating the finely rasped or shredded celluloid with ether, chloroform or other volatile solvent at a moderately warm temperature. Under this treatment magnesia, ammonium phosphate, lead borate or other ingredients are left behind, whilst nitro-cellulose (gun-cotton), camphor, fatty oils or paraffin wax pass into solution. The examination and determination of the insoluble residue is performed on the ordinary analytical lines, though some difficulty is interposed by the organic compounds latterly employed instead of camphor. The examination of the solution is rather difficult, but the nitro-cellulose can be determined by converting it into ordinary cellulose by means of reducing agents. If nitro-cellulose be treated with a concentrated solution of ferrous chloride and an addition of hydrochloric acid at 100° C., nitric oxide gas is evolved, the precipitated iron hydroxide is redissolved in the hydrochloric acid, and structureless cellulose is left behind. According to Hadow, a similar reduction is effected in the case of gun-cotton by treatment with an alcoholic solution of sodium sulphydrate, the precipitated cellulose being then carefully washed with alcohol, dried at 100° C.

and weighed. The determination of nitrogen in celluloid can probably be effected by the method employed by Walter Crum for the nitrogen of gun-cotton. A weighed quantity of gun-cotton is treated with an equal quantity of concentrated sulphuric acid in a tube filled with mercury. The reaction liberates nitric acid, which acts on the mercury and oxidises a portion of same, nitric oxide gas being given off.

After the reaction has continued for several hours, the volume of the nitric oxide gas is read off in the graduated glass tube, and a solution of ferrous sulphate is added; this absorbs the nitric oxide gas, the amount of which is indicated by the shrinkage in volume in the tube.

Celluloid being soluble in boiling caustic potash, certain of its constituents can be determined in this way, the presence of phenol, for instance, as a substitute for camphor, being indicated by the smell it gives off under this test.

Camphor also can be detected by the smell, but the quantitative determination is more difficult. An approximate determination can probably be obtained by boiling the finely powdered celluloid in water until the smell of camphor has vanished, the camphor itself having been carried off by the steam. The fatty oils, fats, etc., incorporated with celluloid can be detected by saponifying the residue from the preceding test with caustic potash. This converts the fatty acids into soluble soaps that can be separated in the usual way. Mineral colouring matters will be found in the residue from the solution in ether, whilst the dissolved colouring matters must be detected by their chemical reactions or physical properties.

CHAPTER VI.

APPLICATION AND TREATMENT OF CELLULOID.

CELLULOID is used for a great variety of purposes that are constantly being extended, there being now few if any industries in which this substance does not find employment in some form or other. In its natural condition, without the addition of colouring matters or other adjuncts, celluloid is very extensively used, especially as a substitute for horn, emery, tortoise-shell, coral, malachite, lapis lazuli, marble, ebony, yellow or black amber, bronze articles, caoutchouc, ebonite, etc.; and in fact there is hardly a single substance known but what attempts have been made to imitate it with celluloid. For the above purposes it is used to a very large extent, and many articles of fancy ware, ornaments, hardware, etc., are of celluloid. In many other branches, too, celluloid has found application, such as artificial teeth, flexible mirrors, decorations in the greatest variety, spectacle frames, watch cases, buttons, pipe mouthpieces, cigar-holders, ash trays, etc.

In fancy goods and hardware celluloid is used for making brooches, hairpins, bracelets, chains, earrings, crosses, medallions (either by itself or in combination with inlaid or riveted metals), imitation horn, tortoise-shell, coral, ivory, etc. It is also made into smooth, inlaid or stamped buttons, knife handles, prayer-book and album covers, cigarette cases, notebook covers, travelling cases, shoe eyelets, purses, pen and pencil cases, rulers, drumsticks, finger-stalls, serviette rings, cigar-holders, dolls' heads and bodies, mirror and picture frames, figures for games, stick, umbrella and whip handles (in a great variety of shapes and patterns that compete keenly with handles of other materials), billiard balls, chessmen and other figures used in games, etc.

For fans celluloid is a somewhat expensive material, but is nevertheless used.

Caoutchouc Industry.—Celluloid is used to a very large extent as a substitute for horn and hard rubber for making plain and fancy combs. The Mannheim Celluloid-waarenfabrik, for example, has laid down an expensive plant for making toilet combs, and can turn them out at a price below that of the small maker who cannot afford such costly machinery. Celluloid combs are beautifully soft, elastic and durable, and share with tortoise-shell the advantage that, when broken, they can be repaired, equal to new, by welding. Within the last few years celluloid balls, which are very elastic and in good demand, have been put on the market.

Makers of fancy wooden articles have taken kindly to celluloid, which they use largely in different forms for covering and inlaying boxes and other fine work.

In the machinery and building trades, again, there is a large consumption of celluloid for emery discs, packing rings, tubes, valves, taps, pistons. It is used in coach-building for making axle bearings, since it is not corroded by oil and therefore forms also a good material for axle-box covers.

In railway work celluloid is used in the form of washers and rings for tightening up fishplates.

Since celluloid can be produced in discs or plates of any desired size, it is used as a stopping for flooring that is desired to be watertight, especially in ships and boats; in the former, indeed, it has also been proposed as an external coating to prevent the growth of parasites.

In dentistry the use of celluloid has attained considerable importance for the manufacture of gum plates.

Opticians employ celluloid for spectacle frames, lorgnettes, mounts for magnifying glasses and opera glasses, just the same as horn, tortoise-shell or caoutchouc.

In brushmaking use is also made of celluloid to a considerable extent, since it possesses the great advantage over wood and other materials that it does not warp in the wet. Latterly also hog's bristles have been replaced by stiff celluloid threads.

Art is also finding employment for celluloid, inasmuch as this substance—so far as present experience goes—may be regarded as a durable ground for painting.

In medicine celluloid has been proposed, and used, as a material for surgical bandages.

Celluloid has, moreover, been used as a material for stamps and printing blocks, and proposals have been recently made to employ it as a substitute for type metal. In this latter connection, however, there is no practical experience at present available as to its utility. On the other hand, it has proved an admirable substitute for stiff collars and cuffs, especially for travellers and pedestrian tourists in summer, owing to its clean white appearance and being impervious to perspiration and wet. The celluloid used for this purpose looks like well-stiffened linen, is flexible, and can be worn for months, being easily cleaned with soap and water. It is also suitable for protective collars on uniforms and as a substitute for cloth facings that are exposed to much wear.

As a leather substitute celluloid finds application for coating harness, buckles, etc.

Being readily soluble in certain volatile solvents, and insensitive to moisture, celluloid has made its way into varnish making, especially for varnishes intended to protect metals from rust and oxidation. This same property is utilised in the manufacture of waterproof fabrics, in place of calico, for bookbinding; but celluloid is too combustible to be recommended for this purpose.

Thus we see that a material which, thirty years ago, was regarded with great suspicion and was denounced as inflammable and dangerous, has taken a premier place in many trades and industries; and since its price is now moderate, its sphere of application will continue to increase—as is shown by the innumerable patents taken out.

As already mentioned, the exceeding plasticity of celluloid in a warm state renders it very easy to make up into various articles; and it can be turned, bored, filed, etc., in precisely the same way as the ordinary materials worked by the turner. Even a temperature of 75° C. makes celluloid plastic enough to be moulded into any desired form in the press, though, as a rule, workers in celluloid heat it to about 120° C., at which temperature it is, of course, much more plastic than at 75° C.

The matrices in which the pressing is done must have been warmed beforehand. The celluloid, warmed to 120° C., is placed in the matrix and subjected to considerable pressure, until the mould has cooled (cooling water is not always required), and the material is fixed in its new shape.

In cutting celluloid, and in all other operations where it has to be worked with iron tools and at high speed, it is advisable to allow drops of water to fall on to the point where the cut is being made. For articles that are to be beaten or pressed out, the celluloid is preferably warmed in water to 40° C., in order to prevent splitting and tearing. If the celluloid has grown too brittle to work easily, it should be dipped in spirit of camphor for a short time.

Owing to the solubility of celluloid in various liquids, it can be easily stuck on other materials or upon other celluloid. An adhesive for this purpose is formed of a mixture of 1 part of shellac, 1 part of spirit of camphor, and 3-4 parts of alcohol. In addition to collodion, pure, finely shredded celluloid dissolved in absolute alcohol makes a good celluloid cement.

To facilitate the escape of camphor vapours from finished articles, these should not be stored in closed boxes or cases.

An important part in the working up of celluloid is played by the moulds, both those used for pressing the celluloid sheets and rods, and those in which celluloid is treated in a more or less fluid condition.

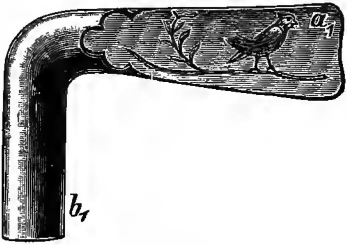


Fig. 24.

These moulds are generally of metal (steel, brass or similar alloys), and contain all the variations of contour of the finished article, so that no after treatment will be required. These moulds, which are more or less elaborate, according to the nature of the article, are expensive, and attempts have therefore been made to construct them of other materials. Mendelssohn, of Leipzig, uses wooden moulds, which possess the great advantage that they can be employed for pressing or blowing celluloid without any previous warming, the wood being a bad conductor and therefore not withdrawing heat from the celluloid.

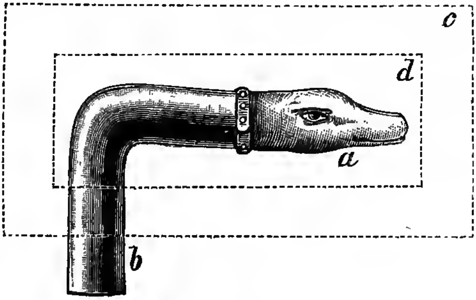


Fig. 25.

Figs. 24 and 25 represent specimens of pressed articles, while Fig. 26 is a longitudinal section of a wooden mould. To press or blow celluloid articles, especially handles for umbrellas, sticks, etc., without any previous warming of the moulds, block or rod celluloid, of suitable thickness, is immersed in boiling water until it is warmed to 100° C., and is then bent into a shape corresponding to that of the mould, *b*, as shown at *a* and *a′*. It is then placed quickly between the two halves of the mould, *c*. If the article is to be solid, the two halves of the mould are pressed together in a suitable manner. Hollow articles are made by admitting steam or other press fluid into the mould containing the (tubular) celluloid, thus forcing the latter into all the contours of the mould. In contrast to metal moulds, which have to be warmed up again each time they are used, wooden moulds can be employed over again in quick succession without taking them out of the press, the low conductivity of wood preventing the celluloid from being robbed of its previously accumulated heat.

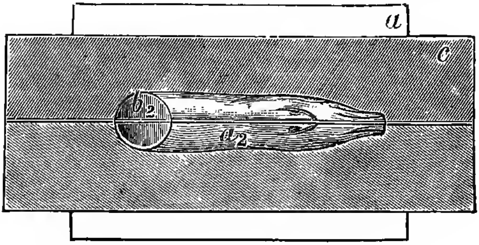


FIG. 26.—Wooden Mould for Celluloid.

The wood used for moulds is moderately hard, such as oak, beech, etc.

According to R. Stübling, cheap and useful moulds can be made from wax models by the electro method, a coating of copper being deposited on the surface of the wax, the latter then removed by melting and replaced by molten alum. The copper deposit is strengthened by a coating of nickel, which is rubbed over with oil, a wax cast being then taken of each half, the outer side of the mould being backed with clay. These wax casts are rubbed over with graphite, to form a conducting surface, and a fresh electro is made, this being filled with plaster of Paris and employed as matrix for a mould of fusible metal.

MAKING CELLULOID ORNAMENTS.

For this purpose the celluloid is made up into sheets, one-twenty-fifth to half an inch thick, and about 12 inches wide by 30 inches long; rods about 40 inches long are also used to some extent. The celluloid used is either perfectly transparent, yellowish and horny, or in the form of imitations of coral, malachite, amber and tortoise-shell. There are two methods of working:—

(*a*) *Working by the Cold Process.*—The sheets are cut up in suitable pieces with a circular saw, and the pieces worked to pattern with fret saw, graving tool, file, or turned on the lathe, to form brooches, earrings, pins, medallions, bracelets, etc., being finished by grinding them smooth with finely powdered pumice and fat, by means of quick-running discs of buckram or carpet fabric, and finally polishing with a buffing wheel and levigated chalk.

The majority of articles are then ready for piecing together and mounting, the various parts of a brooch, earring, etc., being screwed together, fitted with pin or hooks, packed, and sent out for sale.

To save material and time in the case of brooches or other articles representing twigs or sprays of coral, these are cut out of thin sheet material and finished on the flat as above, after which they are made soft and flexible by immersion in boiling water for a few seconds, and the leaves, coral twigs, etc., bent in various directions by hand, being set in their new position by rapid cooling in water. Were it not for the flexibility of the celluloid, such articles would consume fully three times as much material and time in the making. Similarly, bracelets are made of straight, flat strips, and after being polished are softened in hot water, bent round a circular block into the desired shape, and then cooled and dried.

(*b*) *Working by the Warm Process.*—This process entails the use of:—

1. Metallic heating plates, kept hot by means of petroleum, gas, or best of all, steam.
2. Presses.
3. Moulds or matrices of steel or red brass.

The sheets of celluloid are softened on the hot plate, and cut into suitable small pieces with a knife. The pieces, rendered perfectly plastic by heating to a temperature of about 120° C., are next laid in the well-warmed moulds, and kept under a fairly powerful press until the mould has cooled somewhat, whereupon the article is taken out of the mould and cleaned, polished and mounted. Metal ornaments laid in the mould will incorporate with the celluloid thoroughly during pressing. Articles formed in this way lose their shape entirely when reheated; consequently this process is not adapted for the production of strips for bracelets, since the latter would lose the shape imparted in the press on being warmed in hot water for the purpose of shaping them to the arm as described under the cold process.

Celluloid Combs.—These combs are made in the same way as horn combs, so that any one accustomed to work in horn can make celluloid combs, provided he understands how to polish this material.

There is, however, one important particular in which the two processes differ, to the advantage of celluloid, namely, that the troublesome preliminary treatment necessary in the case of horn is dispensed with. The extent of this advantage can be realised by considering the various stages of making horn combs up to that of cutting the teeth. The hollow part of the horn has first to be cut crosswise into lengths, these in turn cut lengthwise, and each strip boiled in water for some time to soften the horn, after which they are fastened on the heating stick, held over a fire and kept turning, in order to heat them still further.

Next come the processes of spreading out flat, scraping to uniform thickness, pressing, splitting, smoothing in the press, etc., all of which are unnecessary in the case of celluloid. The combmaker buys his plates or sheets of the proper thickness, saws them into suitable sizes and smooths out any irregularities by warming the pieces under gentle pressure. Even in the cutting process celluloid presents several advantages over horn, the pieces of the latter having to be clamped on the slope and the saws accurately guided, in spite of which the horn frequently splinters or breaks, whereas none of these inconveniences arise with celluloid. The latter shares with tortoise-shell the useful property of being weldable when broken.

Cutting is effected by hand or machinery, just the same as with horn or ebonite, and the same processes are used in finishing. The combs are polished with pumice and tripoli powder, by means of sticks covered with woollen cloth. Water is allowed to drop on the comb, to keep it from getting too hot and softening, or decomposing and giving off fumes.

Fancy combs of celluloid are bent after softening them in hot water, though some makers bend them over a charcoal fire.

Cheaper combs are made in pairs, the hard-dried thick plates being warmed and the teeth cut in a stamping press. The combs made in this way, however, have merely plain, unornamented backs, and the teeth are devoid of taper; and even softening the plates in water before pressing in moulds, or hot-pressing soft, undried celluloid in moulds, will not give perfect combs. This disadvantage has been overcome by taking the fresh, plastic celluloid plates direct from the cutting machine, pressing them into the form of comb plates (tapered teeth and ornamented backs) in moulds, either in a cold or gently warmed state, and immediately cutting, filing or stamping out the teeth, without drying the mass, which in this condition is easy to work, does not injure the tools, and gives a perfectly smooth-cut surface. The finished combs are then dried in a suitable apparatus to prevent the teeth warping ; and this process enables combs of various shapes to be made. The comb and teeth dry quickly and hard, and become very strong.

CELLULOID AS A BASIS FOR ARTIFICIAL TEETH.

Teeth of bone, ivory and walrus tusks have been displaced by gold, platinum and palladium plates set with enamel teeth. Hard rubber has also been used, but is attended with numerous disadvantages, notably symptoms of mercurial poisoning; and traces of this metal have been discovered in the urine and saliva of persons using hard rubber teeth setting, which has also been known to give rise to disorders, such as salivation, diarrhœa, inflammation of the gums, etc., which disappeared when the rubber plates were discarded. The cause of the trouble was the vermilion used for colouring the plates; but no evils of this kind attend the use of celluloid plates, although these latter are sometimes coloured with vermilion, and it must therefore be assumed that the colouring matter is retained more tenaciously in the mass than is the case with rubber, the saliva being unable to dissolve it out of the celluloid.

Other advantages of celluloid include the possibility of colouring it in exact imitation of the gums, which could not be done with hard rubber. Celluloid is also easy and safe to work, whereas the vulcanising stoves for hard rubber have repeatedly been known to explode.

Celluloid can be used in dentistry both for making the plates and also for entire sets of teeth. A solid mould (usually of gypsum) is made from the wax model, and into this mould the celluloid, in a softened, warm state, is pressed or injected. Various appliances have been devised for making celluloid teeth.

Jüterbogk's apparatus, which closely resembles the vulcanising apparatus used for caoutchouc teeth, consists of a casing, on which is mounted the mortar-shaped steaming vessel containing the mould. The mould clamp is held in position by a device inside the steamer in such a manner that it cannot move when the clamping screw is being turned. The steamer is covered with a simple lid, provided with a hole for the passage of the clamping screw of the mould, and a fitting to hold the thermometer. The pressing temperature is 150° C., at which heat celluloid is plastic throughout its entire mass.

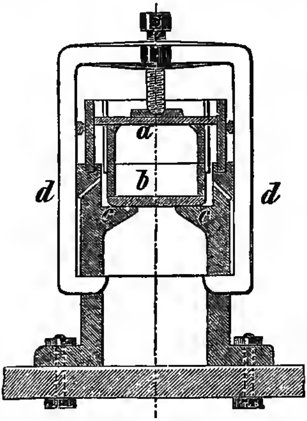
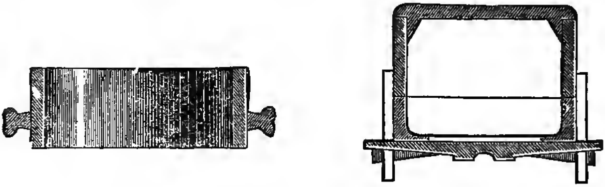


FIG. 27.—Hamecher's Apparatus.

Hamecher says of his apparatus for making artificial teeth plates that all the existing apparatus for treating celluloid for dental purposes have in common the features that the mould is arranged in a vessel or pan heated from the outside, and the celluloid is rendered plastic in the mould and then pressed. His apparatus was based on the idea of avoiding the risk of explosions of the steaming vessel, by dispensing with a steamer and heating the mould itself. It was necessary to pay great attention to regulating the flame, in order that the same, however large, should not rise above a certain height, the level in all cases being below that of the celluloid to be pressed. This apparatus is shown as a vertical section in Fig. 27. A hollow cylinder, mounted on three symmetrically disposed feet, is provided internally with three projecting vertical and radial lugs, *c*, supporting the mould in such a position that the top of the lower half of the mould is on exactly the same level as the upper edge of the cylinder. In order to hold the upper half of the mould in exact vertical register with the lower half, the latter is provided with three wrought-iron guides, two of which are narrow and the third broad, and the upper half carries three guides accurately fitting into the others. The casing (Fig. 28), a cast-iron ring with two handles of wood, is high enough to overtop the open mould, and fits into an annular groove in the top of the cylinder, so as to form an extension of the latter. When the mould is in position the cover fits exactly into the casing. The flame is arranged so that the burner is outside the cylinder, and consequently an ample supply of oxygen is admitted. On the other hand, the flame would only reach the bottom of the mould were it not for the provision of a number of draught holes, *d*, sloping inward and upward through the wall of the cylinder, which they penetrate at a point about half an inch below the upper edge of the top half of the mould, so as to permit the



FIGS. 28 and 29.—Hamecher's Apparatus.

passage of the flame up to the level of the said holes. At the same time the whole of the space between the flame and the lid of the mould is warmed, and after about twenty-five to thirty minutes from the start the thermometer registers 150° C., the necessary temperature at which the mould is screwed down.

The *modus operandi* is as follows. A wax model is made of the teeth or plate, and a plaster cast taken of the model, the wax being melted out with hot water when the plaster has set hard. A piece of sheet celluloid the same length as the test plate is placed in the mould, which is then closed. To collect any celluloid escaping when pressure is applied, a channel about $\frac{1}{25}$ to $\frac{1}{12}$ of an inch deep is arranged, preferably in the top half of the mould, but not in any way connected with the model. When the mould and casing have been placed in position, the thermometer is inserted and the lamp lighted, care being taken that the flame is not too small, but large enough to cover the entire space under the mould. It often happens that the thermometer quickly indicates a temperature which, however, is not attained by the mould in less than twenty minutes; but this should not lead one into error. After a short time all disturbances will have ceased, the water vapour being expelled from the plaster, whereupon the thermometer will give the correct reading. The desired temperature (150° C.) will be attained sooner or later, according to the intensity of the flame, whereupon the mould may be screwed down, all that is necessary being to first extinguish the flame and remove the thermometer. It is necessary to put out the light, or the celluloid expressed from the mould may take fire. The screw is turned quickly, the upper surface of the mould cover being watched to see if it remains horizontal. If it is found to tilt the screw is reversed, the casing taken out of its groove and the mould pushed in the opposite direction so as to equalise the pressure.

When the celluloid offers too much resistance, the mould should be opened a little way (about $\frac{1}{8}$ inch) and left in that condition for one to three minutes before pressure is again applied. The hot plaster will by that time have warmed the celluloid sufficiently to make it much more plastic, as will be evident by the screw turning more easily. If the mould still does not close completely, it is left a few minutes longer and the screw again turned. About ten minutes after the mould has been closed up, the plastic mass will have begun to contract, the pressure will diminish and the molecules draw closer together. The mass hardens, and pressure is applied only at intervals (3-4), after which it becomes unnecessary to press any more.

If the apparatus is to be used over again at once, the mould is wedged properly and lifted out of the apparatus. It is preferably left for half an hour after pressing, and then cooled rapidly by dipping in a pail of cold water, or holding it under a tap. When the outside is cold, the bottom is removed and the temperature of the plaster ascertained. If this is sufficiently low the cover is taken off, and the lower part of the mould is tapped with a hammer several times, causing the whole of the plaster to fall out, with the top half of the mould, whereupon the plaster is broken and the moulded article exposed. Any adherent particles of plaster are picked out with a knife, but it rarely happens that the article needs to be touched up with the file or graver, all that is necessary being to rub it over with fine sandpaper and polish with oil, soap and levigated chalk.

STAINED CELLULOID SHEETS AS A SUBSTITUTE FOR GLASS.

Thin celluloid sheets can be stained superficially, on one or both sides, by dipping them in a bath of coal-tar dye, prepared by pouring an alcoholic solution of the coal-tar dye into a bath of 99 per cent. spirit containing best white shellac and sandarach, or some other resin. This bath is acidified with boric acid, and shortly before use a little ether or benzol is added, to accelerate the drying of the coloured layer on the surface of the celluloid.

The celluloid sheets are immersed for a short time merely, this being sufficient to mordant and colour the surface. The coloured layer dries very quickly. If only one side of the sheet is to be stained, the other is first coated with asphaltum in the usual manner. These coloured sheets are suitable for signals and identification devices, being unbreakable and fast coloured.

CELLULOID PRINTING BLOCKS AND STAMPS.

The reproduction of woodcuts by means of celluloid presents numerous advantages, the plasticity of this material enabling it to penetrate the minute depressions of the pattern block, and furnishing an accurate reproduction of the woodcut, even superior to electros, owing to the absence of the intervening layer of graphite. The method adopted is as follows. A cement cast is taken of the woodcut, this material being easily detachable without injuring the reproduction, and serving to replace gutta-percha. This cement casting is placed in contact with a softened sheet of celluloid in a hydraulic press, and in five to six minutes the celluloid will have been forced into even the finest parts of the mould. The entire operation takes only half an hour. The celluloid is superior in many respects to an electro block, as it stands the pressure better in quick-running presses, and is said to yield over 100,000 impressions.

Celluloid stamps are very elastic and durable, the wear being small; and they are superior to rubber stamps inasmuch as any kind of stamping ink can be used without risk of corrosion by the colouring matter. They are very easily made, a sentence set in type, or a mould (letters, pictures, ornamental devices, etc.) cut in wood, being laid on a flat surface, preferably of hard wood or stone, and covered with a moulding frame a little smaller than the mould, in order that the edges of the frame may fit closely.

The inner sides of the frame slope inward, so as to support the plaster cast when the frame is raised; and the long sides are provided with recesses for the insertion of the lifting tool.

All parts of the mould that are to be covered with plaster are oiled with a small soft brush, so that even the spacing leads and quads are properly coated. The oil for this purpose is made by mixing 32 parts of bone oil, 32 parts of oil of turpentine, 1 of cotton-seed oil and 1 of white copal varnish in the warm.

Finely ground, freshly burned stucco plaster is used for the casts, and this is made up to a thick pulp with clean well-water in a suitable pail, the mixture being poured on to the surface of the mould so as to barely cover it. This is now worked into the lettering by means of a stiff brush, so as to fill up all the depressions in the mould, and a fresh quantity of plaster is poured in until it begins to run over the edges of the frame, the surplus being brushed off with a straight edge after settling. In five minutes the plaster will have set hard enough for the frame and matrix to be taken off the mould by means of the lifting tools.

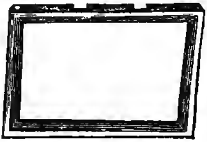


FIG. 30.—Mould Frame.

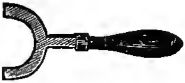


FIG. 31.—Lifting Tool.

A gentle tap on the forme holding the mould will loosen the plaster from the mould, and the frame and plaster cast can be lifted by means of the tool illustrated in Fig. 31, the points being inserted in the recesses in the frame (Fig. 30). A gentle tap on the frame will detach the plaster matrix, which can be transferred shortly after to a drying apparatus.

This consists of a strong sheet-iron stove, with a fire in the lower portion, so disposed that all parts of the plate supporting the drying frame are heated uniformly. The upper part of the stove is fitted with a drying rack, of one or two stages, the fresh matrices being placed on the lower stage, whilst the upper one is for final drying. The drying rack consists of an iron plate, from which project twelve to fifteen iron-wire arches, about an inch apart. The matrices are placed between these wires so that the fronts and backs are exposed to the ascending heat. To ensure uniform drying, the matrices have to be turned at frequent intervals, otherwise they would warp from uneven drying and break in the press. With a good fire a stove full of matrices will dry in about four to six hours. If there are two stages, the matrices are taken off the bottom one at the end of that time, and placed on the upper rack, the other being recharged with a fresh supply. When the matrix has assumed a whitish yellow colour, and rings on being tapped on the back with the finger, it is properly dried. The slightest trace of moisture in the middle of the mass renders the matrix liable to break in the press, or to furnish a poor stamp.

The dried matrix is brushed over several times with a thin solution of shellac, to give it a smoother surface and greater durability, a point of considerable importance in the subsequent pressing.

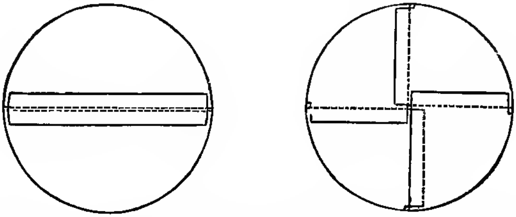
The matrix is now a yellowish white block of varying thickness, and containing an impression of the letters in their right order. The depth of the impression corresponds to the height of the original design on the type-block or woodcut, whilst the remainder should form a flat, even surface if the stamp is to be of any use.

To prepare a stamp from this matrix, a sheet of celluloid is cut to the proper size, the piece being then placed in a water bath, at 70° C. exactly, for ten minutes, until the celluloid is thoroughly softened. Meanwhile, the press has been got ready, the mould placed on the loose table, the celluloid is taken out of the water, quickly laid on the matrix, and the table is pushed into the press, the latter being started at once. After being in the press five minutes the table is drawn out again, and the celluloid will be cold enough to be taken out of the mould without injury. It would be an improvement to jacket the press and raise it to the requisite temperature (70° C.) by means of steam or hot water. With this arrangement a number of moulds, containing the celluloid sheets, could be inserted into the space inside the press, and on attaining the proper temperature be pressed for five minutes and taken out again.

The softened celluloid is forced into all the depressions in the matrix, just the same as in making rubber stamps, so that the design appears in reversed, raised letters, etc., on the face of the celluloid. On cooling, the latter resumes its original hardness, and the plate can be glued or cemented on to the handle of the stamp.

Collapsible Seamless Vessels of Celluloid.—Collapsible tubes of celluloid are difficult to make, since the material cannot be brought into the form of a sufficiently thin, flexible and compressible tube. Vessels manufactured from thin sheet celluloid soon become brittle and inelastic, especially when they are kept in contact with hygroscopic substances, such as toothpaste, etc. To make these tubes and other hollow articles, a cylindrical incompressible core is dipped repeatedly into dissolved pyroxylin until sufficiently coated; the coating is dried, and is then drawn off the rigid core by the combined assistance of heat and moisture, which help it to come away easily. The material used (a solution of celluloid in amyl acetate) is insensitive to the action of moisture, dilute acids and alkalis, whilst at the same time it is strong, very flexible and elastic, and does not lose these properties after being in contact with hygroscopic substances. The material is so thin that the tube will return to its original shape if pressed when empty, but will remain flat after being pressed when full. The core employed is a glass tube of the desired form and size, and provided at the lower end with a tapering screw neck. The finished tube is detached from the core by dipping it in water, or treating it with steam. The screw cap is made of aluminium or other metal. After filling, the open end of the tube is bent over and fixed with a metal clip.

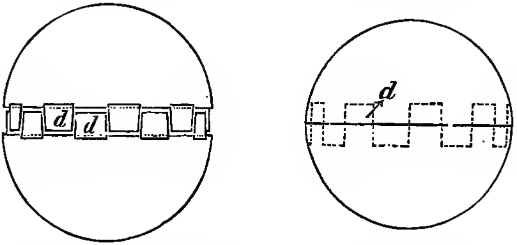
Making Celluloid Balls.—Celluloid balls made by the older method of cementing together two hemispherical cups had the defect of soon coming to pieces, to remedy which it was proposed to fit the joint with a protecting strip (Fig. 32), or to divide the ball into several sections, *e.g.*, four, with overlapping edges (Fig. 33). Even these methods of joining, however, proved unsatisfactory and liable to come apart after a time, in addition to which the former is difficult to carry out, and the second both troublesome and expensive. Applied to hemispherical cups, the second method offers no advantage over the underlay strip, and there always remains a noticeable depression at the joints, so that none of these methods properly meets the requirements of practice.



FIGS. 32 and 33.—Ordinary Method of Joining Celluloid Balls in two or more Parts.

The following method, however, furnishes a joint which is not only durable, but fits as true as though the ball were made in one piece. Each half of the ball is toothed at the edges, and the teeth are pressed inward at right angles, and bent again at a distance corresponding to the thickness of the sheet, while the celluloid is plastic, the two halves being then pressed together so that the teeth in each half fit inside the other and make a very firm joint, especially when fastened with a suitable adhesive. Fig. 34 shows the two halves of such a ball, before and after being assembled, whilst Figs. 36-38 represent the press employed.

This press consists of the mould, A, and die, B, the latter being fitted, above the hemisphere, with a ring, C, the lower end of which is recessed in the form of teeth. The thickness of the tooth-shaped projections, D, must be calculated so that their outer surface fits exactly in the upper cylindrical part, *a*, of the mould. The teeth are preferably made somewhat tapering in the width and a little wider than the gaps in the ring, C. This latter may, of course, be also made in one piece with the die.

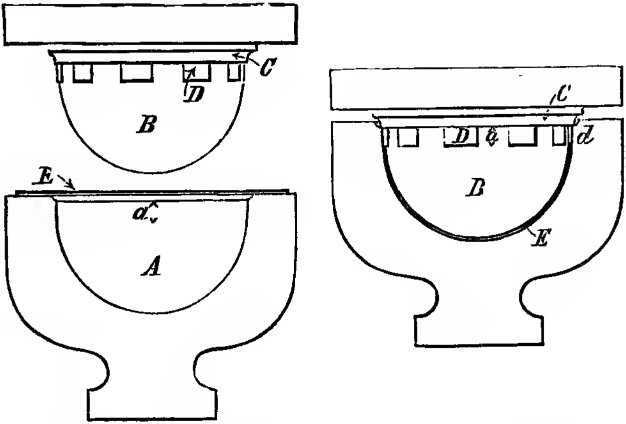


FIGS. 34 and 35.—Toothed Joint for Celluloid Balls.

The celluloid sheet, E, is pressed while in a plastic state, by placing it on the mould, A, and forcing it into a hemispherical shape by the die, B. The edge of the sheet coming into position in the cylindrical part, *a*, of the mould, is cut into teeth by the teeth, D, of the die, these teeth remaining attached to the half ball and being a little narrower at the top than the gaps left between them.

The halves are taken out of the mould, the cuttings removed, and the teeth made plastic and then bent inward in the shape of a crank corresponding with the thickness of the shell of the ball. The halves are brushed over with a suitable adhesive and put together so that the teeth on each half fit in between those on the other. The adhesive is applied in such a manner that the edges also of the two halves stick together.

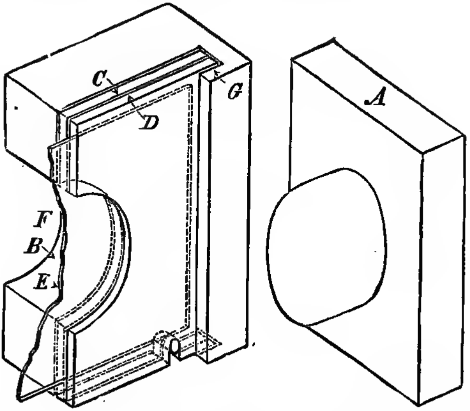
Celluloid Posters.—The celluloid posters or placards now in use consist of a sheet metal backing over which a sheet of celluloid is stretched, and fastened at the edges by insertion into the turned-over edges of the metal. This arrangement has the defect that the celluloid, sooner or later, comes undone at the edges and springs off. In the newer makes this defect is overcome by a better method of folding the edges, namely, by doubling the metal and celluloid over twice or more.



FIGS. 36, 37 and 38.—Pressing the Halves of Celluloid Balls.

PRESSING HOLLOW CELLULOID ARTICLES.

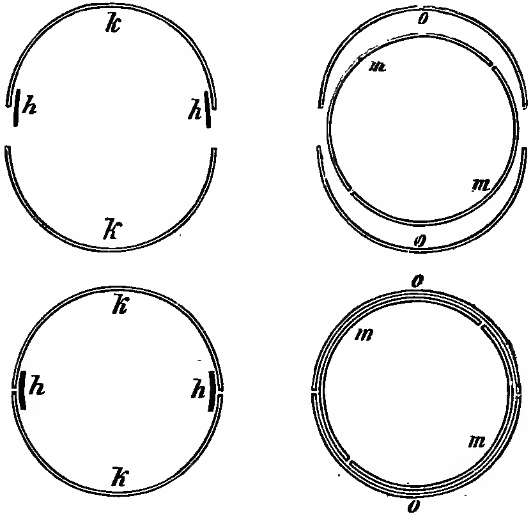
When divided metallic moulds and dies are used for pressing deep hollow bodies, these parts have to be heated, which results in the drawback that, in order to prevent loss of time in heating and cooling the presses, one attendant must have several sets of moulds and dies available. The production of these moulds and dies, however, is an expensive matter when they are all of one kind; whereas by the newer method, one attendant, with one set of moulds and dies can keep on pressing and turn out five times as many articles in the same time. Moreover, the same bottom die can be used for a number of differently shaped articles, thus reducing the cost of the die considerably. The bottom die (Fig. 39) comprises the block, B, pierced by a cylindrical opening, which may be independent of the shape of the article to be pressed, but must be large enough to take the upper die when the latter is forced down. At the top of the bottom die are two lateral guide slits, to receive the two sliding plates, C and D, and the interposed sheet of celluloid. Both these plates have circular openings corresponding with that in the bottom die, so that the celluloid sheet is left exposed in that part for the action of the upper die, whilst the edge is held between the plates. A is the top die, which, in conjunction with the lower sliding plate, determines the shape of the article to be formed.



Figs. 39 and 40.—Dies for Pressing Hollow Celluloid Articles.

Fig. 39 represents a cross section of the bottom die with the two sliding plates, C, D, and the interposed celluloid sheet, whilst Fig. 40 shows the upper die by itself. In pressing, both the block, B, and the upper die, A, are fixed in the press, neither of them being warmed.

The celluloid to be treated is rendered plastic by heat, and is laid between the two sliding plates, C, D, with which it is slipped into the guides in the block, B, and the upper die is moved down by the press and forces the exposed portion of the celluloid sheet, E, down before it, the edges of E being meanwhile held fast by the plates, C, D. The press is now opened, the top sliding plate is drawn out, the pressed article removed, a new celluloid sheet inserted, followed by the top sliding plate, and the upper die again moved downward by the press.



Figs. 41-44.—Device for Pressing Hollow Balls.

This rapid pressing is rendered possible by the fact that the inner sliding plates give off only just enough heat to prevent the celluloid from cooling too rapidly. At the same time, when the upper die has reached the bottom of its stroke, the celluloid has cooled sufficiently to retain its new shape. The block, B, is gradually warmed by the sliding plates, but this has no effect on the operation, since the opening in the bottom die is so wide that it does not come into contact with the pressed article.

To enable celluloid sheets of different thickness to be pressed, a spring is provided inside the guide slit or under one of the sliding plates, to hold the two plates in sufficient contact.

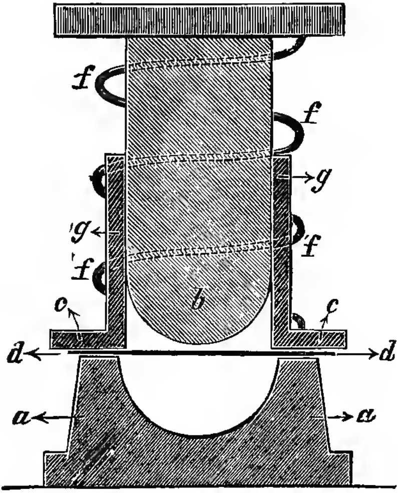


FIG. 45.—Press for Hollow Celluloid Balls.

In the method employed by the Rheinische Gummi- and Celluloidfabrik, Mannheim, two hollow balls are made in an ordinary screw or lever press, with a divided wooden or metal mould. A section of one of these presses is illustrated, open, in Fig. 45. In this press, *a*, is the lower half of the mould, and is fixed in the base of the press, *b*, being the die or inner half of the mould, which works up and down with the movable part of the press and fits exactly in the lower part, *a*.

The construction of the three-part mould is already known; but on the other hand the arrangement of the plate, *c* (Fig. 46), is novel, this plate being pressed in any suitable way against the mould, *a*, in order to hold the inserted sheet of celluloid, *d*, uniformly at the edges. This should be one-third larger in diameter than the desired ball.

The plate, *c*, is pressed against the mould, *a*, by the spiral spring, *f* (Figs. 45 and 46). The plate is also fitted with guides, *g*, to prevent slipping. In the absence of this plate, *c*, the circular celluloid sheet would be pressed into the mould, *a*, in innumerable wrinkles instead of forming a smooth hemisphere of uniform thickness.

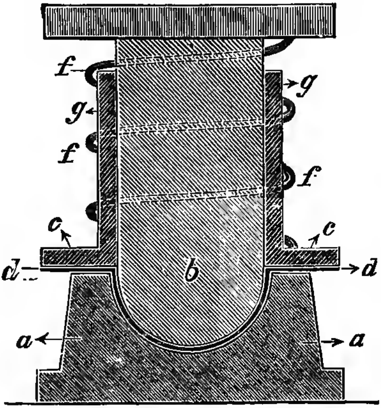


FIG. 46.—Press for Hollow Celluloid Balls.

Fig. 46 shows the press closed, *i.e.*, at the end of the operation; *a* and *b* represent the two halves of the mould, and *d* the sheet of celluloid which has been pressed into a hemisphere between them. During the operation the plate, *c*, is held tightly against the mould, *a*, by the spiral spring, *f*, which is in a state of compression.

When the press is opened, the part *b* rises first, until the spring, *f*, is released, whereupon the plate, *c*, also rises, and enables the pressed hemisphere, *d*, to be taken out of the press.

In fitting the two halves of the ball together, it is not sufficient to merely fasten the edges by means of an adhesive, and the joint must be strengthened by a strip of celluloid inside. The width of this strip (*h*, Fig. 41) is preferably about one-tenth the diameter of the ball, the length being equal to the periphery. The strip is first fastened inside the one hemisphere, *k*, and then cemented to the other.

The two halves may also be cemented on to a smaller ball (Figs. 42 and 44). This inner ball, *m* (Fig. 42), is made of two hemispheres, on to which the outer halves are cemented, *o* (Figs. 42 and 44), care being taken that the joints of the two balls do not coincide.

Casting Celluloid Articles.—A suitable mass for casting is obtained by dissolving 1,000 parts of celluloid in an equal quantity of acetone and adding 250 parts of magnesia, 50 of levigated chalk, 220 of glycerine, 100 of ether and 150 of spirit. This mass runs easily into the moulds and sets rapidly, so that, by drying at 20° C., the article can be turned out complete in three hours.

Method for Producing Designs on Plates or Sheets of Celluloid, Xylonite, etc.—The old method of producing patterns or designs on plates of celluloid, xylonite or similar plastic, nitro-cellulose products, was by printing or pressing, with or without the assistance of warmth, or by moulding and painting. A newer method consists in stamping a design in relief on sheets of white or yellow celluloid, then applying colours or paints, and finally imparting a polish to one or both surfaces by means of suitable rollers or plates, assisted by heat and pressure, this treatment bringing the pattern up more effectively on the polished surface of the sheet.

The mordant and colour can be applied to the printed plate by dipping the latter in a dye bath, whereby the colouring matter penetrates the hollows of the pattern and forms a thicker layer there than on the rest of the surface. The sheet is then subjected to powerful pressure, assisted by heat, between plates, which may be polished or not. The pressure and heat smoothen the engraved surface again and bring into admirable prominence the deeper portions which before were hardly noticeable.

If one side of the sheet is to be polished, a polished plate is pressed against the portion that was not brought into contact with the dye, and this will bring the drawing up prominently on the polished surface, though it was actually impressed on the other. This polish can also be produced on the printed surface, or on both, the result in all cases being to bring out the pattern better.

The impression can be imparted to the sheet by various means, such as wire, cloth, dies, rollers, etc.; and one on both sides of the sheet can be coloured, all over or in parts, by either applying the colour locally with a brush, or dipping the sheet in a dye bath.

Imitation Tortoise-shell.—Celluloid constitutes the most suitable imitation of tortoise-shell that has ever been devised; and imitations of this kind are supplied by celluloid makers as well as being made by consumers. The celluloid sheets employed for this purpose range from $\frac{1}{25}$ to $\frac{1}{8}$ of an inch in thickness. The ground colour of real tortoise-shell is a faint brownish yellow, to imitate which the celluloid is stained with picric acid in the process of manufacture, by means of a solution containing a little aniline brown, picric acid by itself being too yellow.

The reddish brown spots so characteristic of tortoise-shell are imitated by means of an alcoholic solution of aniline brown, with a little fuchsin to bring out the reddish tone. As celluloid is softened by strong alcohol, these solutions penetrate deeply into the mass. The sheets having been highly polished before applying the colouring, the lustre removed by this latter operation is restored by diligent rubbing with woollen cloths. Articles of definite shape, like combs, etc., are not painted until the shaping process is completed. Incrustations of smooth-rolled metal wire, stars of thin leaf gold or silver for expensive cigar cases and purses, small fancy boxes, etc., are pressed into the mass as already described, the latter being then smoothed, polished and finally coloured. When the colouring is applied by a skilled operator it is hardly possible to distinguish the imitation from the genuine tortoise-shell by the appearance.

METALLIC INCRUSTATIONS.

Imitations of metallic incrustations, resembling metallic ornamentations inlaid in ivory (or other material), are produced on a basis of celluloid ivory by the use of real or imitation gold or silver bronze mixed to a thick fluid with collodion. The design having been painted on the celluloid sheet with this medium, the sheet is laid on a perfectly flat, thick zinc plate, and heated to 125-130° C., the two sheets being then passed between smooth rollers under gentle pressure. This pressure is sufficient to force the thick layer of colour or bronze into, and unite with, the softened celluloid. Ornaments stamped out of thin sheet metal can be fixed in celluloid in exactly the same way, the surface of the celluloid being then smoothened by rubbing over gently with powdered pumice, and finally polishing with Vienna lime. If the layer of paint or bronze has been too thick, it can be reduced by rubbing down. In the case of metallic inlays, especially those made with imitation bronzes, it is highly advisable to protect the metal from atmospheric influences by a coating of transparent material, so as to preserve its pristine lustre. For this purpose, thick collodion mixed with camphor solution, is poured over the celluloid, in the same way as in making a collodion plate in photography, the surplus liquid being allowed to drain off at one corner, and the celluloid sheet set up on edge to dry. After several hours have elapsed, the collodion coating is highly polished by the simple method of rubbing it with a woollen rag.

IMITATION FLORENTINE MOSAIC.

Real Florentine mosaic work consists of cubes of marble or other coloured stone set together to form pictures (figures, ornaments, flowers, geometrical figures, etc.), and generally inlaid in a plate of plain marble. The laborious method of production renders genuine mosaic work very expensive, which explains the desire for a good imitation. The celluloid is used in the form of sheets not more than $\frac{1}{25}$ inch thick, and stained in the colours to be reproduced in the picture. The sheets should all be rolled in the same mill, so as to preserve uniformity of thickness. A large number of punches or dies of various shapes, with sharp cutting edges, are used for cutting out the tesserae.

To imitate, for instance, a mosaic picture in several colours on a black marble ground, the contours of the picture are cut with punches out of a sheet of black celluloid, which has been softened by warmth to make it plastic and thus prevent the cracking that would occur in punching out a sheet of the ordinary hardness. For this purpose the sheet is laid on thin boards that are covered with thick sheet lead, and is warmed to about 120° C. At this temperature a sharp cutting tool will punch the plate under the pressure of the hand. The cut out pieces are laid carefully on one side, as they can be put to further use. The same cutting tools are employed to cut corresponding pieces out of other coloured and softened sheets of celluloid, a sufficient number of each being prepared to enable a large quantity of mosaic pictures to be put together at one time. This is essential owing to the high cost of the punches for each picture.

In assembling the picture the spaces cut out of the ground plate by the different punches are filled with pieces of corresponding shape and size (cut by the same punches), which fit accurately, their colour varying according to the requirements of the picture. For this work the plate must be laid on a thick and perfectly flat zinc plate, the finished picture being covered by a second zinc plate and the whole warmed to 100° C., whereupon it is passed through smooth rollers under very gentle pressure and set aside to cool. The warmth will have caused the pieces composing the picture to expand so that the edges unite, and this union is strengthened by the pressure employed, so that there are no joints visible between the pieces, and the whole picture, built up of many parts, has become as one. The picture is then rubbed quite smooth with powdered pumice, and polished with Vienna lime. If carefully made, it forms such a perfect imitation of a genuine Florentine mosaic picture that the difference can only be detected by careful examination. To fasten the mosaic sheet on a backing of slate or wood, the surfaces to be fixed together are roughened and coated with a liquid prepared by dissolving 10 parts of shellac and 5 of camphor in 40-50 of alcohol. They are then laid in contact and subjected to gentle pressure for several hours, by which time they will have firmly united.

CELLULOID COLLARS AND CUFFS.

These are made of sheet celluloid, not more than $\frac{1}{25}$ inch thick, that has been whitened with zinc while in the making. White lead must not be used for this purpose at all, as it would soon turn yellow, and finally grey, under the action of perspiration. The moulds for these articles are made as follows. A well-starched, new, best linen collar (for example) is spread out on a zinc plate, and from it is made a plaster cast which accurately reproduces both the stitching of the seams and the texture of the fabric. A similar cast is taken of the underside of the collar, and from these casts type-metal moulds are prepared. The sheet celluloid, stamped out to the proper shape, is laid in the previously warmed mould, and on pressure being applied, the softened celluloid is forced into all the irregularities in the moulding surfaces and reproduces them. When the mould has cooled, the flat collar is taken out, bent round over a tinned iron pipe heated by steam, and passed between quick-running rollers covered with soft cloth so as to produce a high gloss.

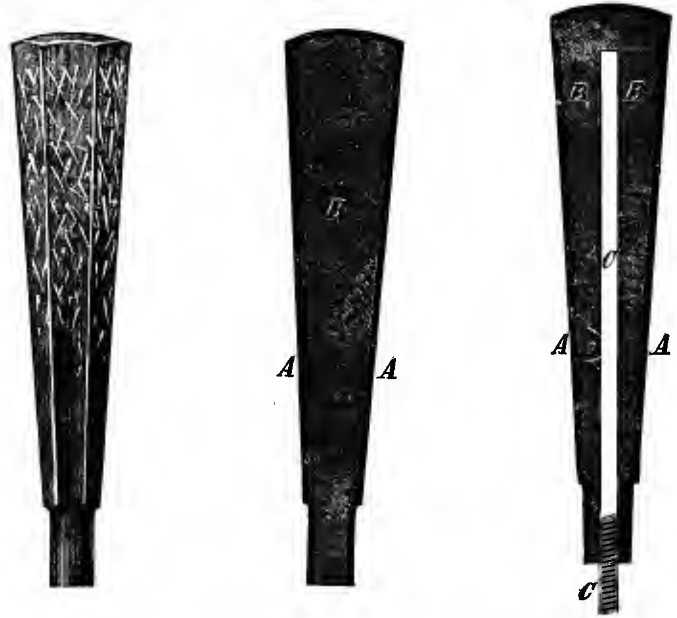
PHONOGRAPH CYLINDER COMPOSITION.

The older method of reproducing original phonograph records on to celluloid cylinders consisted in making an electro from the original record, and inserting in the electro (which carried the record on its inner surface) a celluloid cylinder, which was then warmed and suitably pressed against the electro. These records, however, are not very durable, neither are they sufficiently loud and pure in tone. An improvement is effected by replacing ordinary celluloid by a mixture of celluloid and stearic acid, the cylinders furnished by this compo reproducing the original perfectly, and giving a stronger, more resonant and life-like tone. The stearic acid may be added to the celluloid in the process of manufacture without any other alteration in the composition of the mass.

MAKING UMBRELLA AND STICK HANDLES OF CELLULOID.

The methods of making these articles are too numerous to mention in the space at disposal, but attention may be drawn to that of Schreiner and Siever for imitation "tiger's eye" handles.

These are made of transparent celluloid, A (Figs. 48, 49), hollow and of any shape, the interior being filled with colophony, resin, or any other fusible, brittle material, as at B, and the two ends closed with celluloid. The handle is then tapped gently and shaken, so as to produce innumerable small cracks in the brittle filling. When polished, the handle has the appearance of a solid article of a beautiful and novel colour. The strength of these handles can be increased by a thin core of wood or iron, C, which must not fill up the whole of the interior, but leave enough room for the resin. The method can also be applied to making paper weights, door handles, buttons, etc.



Figs. 47, 48 and 49.—Stick and Umbrella Handles.

Celluloid Dolls.

The parts of the doll are rough pressed, so that there is little strain on the materials, especially at the joints, in finishing. These parts are laid together in a properly warmed mould and pressed, the edges being coated with an adhesive if necessary. The press unites the parts and also cuts off all the surplus material (flanges). The joints and other portions of hollow parts that are most exposed to bending, pressure and other strains when in use are strengthened by backing with small plates moulded to fit the parts and extending a short distance on either side the joints. When these backings are dry so that they will not get out of place in the blowing process, that is to say, when the backed places are as dry as the rest, the rough moulded hollow article is placed in the finishing mould and blown in the usual manner.

CELLULOID FOR SHIPS' BOTTOMS.

A coating of celluloid has been successfully employed as a protection against parasitic growths, etc., on ships' bottoms. A trial sheet about 9 square feet in area and $\frac{1}{16}$ inch thick, quite transparent and free from any mineral adjuncts or paint, was fixed on the bottom plates of a small screw steamer. Examination, repeated annually, showed the celluloid to remain quite free from plant or crustacean growths, whereas the rest of the bottom was so dirty as to need cleaning. After four and a half years the celluloid plate exhibited not the slightest alteration in strength, elasticity or character. Celluloid varnish was not tried, as it necessitates a surface warmed to 36° C. before it can be applied. Owing, however, to the high price of celluloid and the difficulty of attaching it to the ship's plates, the practice will scarcely come into vogue.

CELLULOID PENS.

These are made in France by stamping out thin sheets of celluloid, ebonite, vulcanite, etc., in the form of pens, which are then perforated, and pressed in hot moulds to give them the right shape. After being cooled in water the splits are cut with a knife.

COLOURING FINISHED CELLULOID ARTICLES.

Though celluloid is obtainable in a variety of colours, it is sometimes necessary to stain finished articles another colour. As a rule, coal-tar dyes dissolved in spirit make excellent stains for this material; and for special purposes the following methods are recommended:—

Black.—The article is dipped first in weak alkali, then in dilute silver nitrate, and left to dry in the sunlight.

Blue.—A solution of indigo nearly neutralised with potash is used, or a solution of Prussian blue; or a bath of ferric chloride followed, after drying, by one of potassium ferrocyanide.

Green.—The article is dipped in a solution of 2 parts of verdigris and 1 of sal ammoniac.

Yellow.—The article is dipped successively into a solution of lead nitrate and one of yellow chromate of potash.

Brown.—A solution of potassium permanganate, made alkaline with soda, is used.

Red.—The articles are first dipped in water, slightly acidified with nitric acid, and then in an ammoniacal solution of carmine.

Purple.—Immersion in dilute chloride of gold, followed by exposure to strong sunlight.

PRINTING ON CELLULOID.

For ordinary lettering, etc., or showing up fine coloured lines, celluloid may be printed in the usual way. The material, however, has to be specially prepared so as to obtain a matt or rough surface of suitable grain (by handwork, sand-blast or other means), leaving, if necessary, certain parts of the surface intact. The sheet or plate is swilled with water or alcohol, to free the depressions from any clogging, adherent particles, and is then coated with a varnish made of 2 parts of boiled linseed oil, 1 of white copal varnish and 1 of refined ethereal oil, preferably oil of turpentine or lavender. The varnished plate is wiped to force the varnish into the artificial pores of the grain and leave the surface bare, and is then covered for several hours with a mixture of equal parts of finely powdered magnesium and barium sulphates, after removing which it is carefully satined. This treatment gives a surface containing, enclosed in its innumerable fine pores, a very thin almost transparent layer that exerts chemical attraction on the fatty bodies in printing ink and absorbs and retains them like paper. The most delicate drawings and shades of colour can be printed on this surface without risk of running or clogging.

According to F. Meyer (Bingen) celluloid printing is performed as follows. On the one hand, the desired pattern, etc., is printed on paper or like substance, and on the other, the celluloid is moistened with a known solvent, such as alcohol, ether, etc. On pressing the paper and celluloid together a portion of the ink on the former dissolves out and intimately mixes with the dissolved surface of the celluloid, thus forming a waterproof design.

J. Artner's improvements in printing on celluloid relate more particularly to collars, cuffs and other washable apparel, with the object of protecting the applied colours from the perspiration of the body and friction with other clothes. In contrast to existing methods of printing celluloid, the method adopted is to coat the printed surface with a transparent film, protecting the colours from contact with perspiration, other clothing and from water in washing.

The colours or designs are applied by rollers engraved in relief so that they are printed and pressed in at the same time. The celluloid articles are then dried, and coated by dipping in a warm, transparent hard-drying varnish which dissolves the surface of the celluloid and forms a coating that hardens on cooling so as to prevent the colours from rubbing off.

This method can be applied to all celluloid articles, is simple and reliable, furnishing a product capable in a high degree of resisting external influences. The varnish used is a solution of copal in ether, with alcohol and water, and a trace of oil of turpentine, the proportions being :—

Copal dried at 100° C.	6·48 per cent.
Alcohol	16·40 ,,
Water	1·20 ,,
Ether (sp. gr. 0·725)	75·47 ,,
Oil of turpentine	0·45 ,,

The copal is dissolved in the ether, the solution diluted with the alcohol and water, and the oil of turpentine added last. The ether has a slight solvent action on the celluloid and assists in binding the varnish, whilst the oil of turpentine prevents the varnish cracking off.

The printed and varnished articles are finally dried at 50-55° C.

Neupert (Altona) prints waterproof patterns on celluloid plates by graining the latter with equal parts of wax and potash, together with water, and oil of turpentine if too thick. A pattern applied to this surface by means of an alcoholic solution of colouring matter will partly dissolve the wax (by the alcohol and alkali together) and give a sharp impression. The case is parallel to the result obtained with sized paper in comparison with unsized, the dissolved colour in the present case penetrating with the wax into the pores of the celluloid, whereas the colour would run on the untreated celluloid.

The Rheinische Gummi & Celluloidfabrik replace alcohol by acetic acid for dissolving the colouring matter, and thus dispense with a preliminary treatment of the surface. Probably this is due to the fact that this solvent attacks celluloid and thus penetrates it and dries therein at once.

The running of the colour on certain kinds of celluloid can be prevented by moistening the surface with oil of turpentine or melted paraffin wax.

Employment of Celluloid (and Pyroxylin) in Lacquer Varnishes.

The solubility of celluloid and pyroxylin in more or less volatile liquids, such as ether, alcohol, acetone, etc., was utilised some twenty-five years ago for the purpose of coating metals and other substances with an extremely thin, glossy and flexible layer of celluloid (pyroxylin). These solutions are now sold under various names such as crystalline, Zapon lacquer, Victoria lacquer, etc., and differ from all other lacquers in that whilst they will not give a gloss when applied to paper, wood, fabrics, etc., and destroy the lustre of other lacquers, they do not affect that of polished metal, glass, etc. This characteristic difference is also the reason for their extensive use, the main principle of which is to furnish a lacquer that is barely visible on the object to which it is applied, and does not affect the gloss, porosity, appearance, etc., of the material at all. Now, all resin lacquers, whether oily or alcoholic, show up when in position—the lacquer on polished metal being iridescent by reflected light, owing to the heterogeneous condition of the dissolved resin. On the other hand, the layers of celluloid lacquer are so tenuous as to be invisible, and, if properly applied, they never iridesce on metallic surfaces. They adhere very tenaciously to all materials, and cannot be removed from metal by scraping, though the lacquers themselves are soft and elastic.

All other known lacquers, even those classed as "matt," produce a more or less glossy surface on matt substances like paper, wood, etc. Absorbent substances are rendered stiff and hard by taking up large quantities of the solution. Celluloid lacquers on the contrary do not interfere with the gloss of metal or glass, they leave the properties of paper, wood, etc., unchanged, whilst absorbent substances are left soft and flexible, owing to the peculiar properties of celluloid. It is clear that such a lacquer is suitable for very extensive use, and in fact it can be applied to all manner of objects: to metals (to prevent tarnishing), to cementing celluloid articles, as a fixing varnish for drawings, document varnish, printing lacquer for painting on fabrics, map varnish, playing card varnish, dolls' heads, toys, staining and matting glass, etc. Moreover, it is easy to use, no skill in manipulating a brush being required; and there are no troublesome bubbles, raised edges and drops as with spirit varnishes. The celluloid varnish is either poured on to the article or used as a dipping bath, though celluloid varnishes with slow-drying solvents have now been introduced for brush work, and the combination of various volatile solvents has also enabled matt celluloid varnishes to be prepared. The coatings dry very quickly, and will last for years without cracking or peeling.

Celluloid varnishes are prepared from dry or spongy celluloid, or from nitro-cellulose and camphor. They should be made in well-closed vessels, fitted with stirrers, and heated if possible by steam or hot water. The resulting solutions should be quite clear, or soon clarify on standing, filtration being a difficult matter owing to the volatility and inflammable nature of the material, and the ease with which the pores of the filter are choked.

Acetone, sulphuric ether, alcohol, amyl acetate, amyl hydroxide and various acetic esters, chlorhydrins, etc., can be used, together or separately, as the solvent. One mixture consists of acetic acid and amyl acetate; another of amyl hydroxide and alcohol; a third of amyl acetate and alcohol; a fourth of acetic ether, acetic acid and ether; and a fifth of amyl acetate and amyl hydroxide. Transparent celluloid, swollen by steeping in amyl acetate, will dissolve in equal parts of alcohol and oil of turpentine, and also in amyl acetate, to a clear solution, but gives a matt coating on metal. Celluloid to be dissolved is cut into small pieces, left moistened with alcohol or ether for some hours and then placed in the solvent. The following proportions will give good results:—

1.	Celluloid . .	5 parts.
	Amyl acetate .	16 ,,
	Acetone . .	16 ,,
	Sulph. ether	16 ,,
2.	Celluloid .	10 ,,
	Sulph. ether .	30 ,,
	Acetone . .	30 ,,
	Amyl acetate .	30 ,,
	Camphor .	4 ,,
3.	Celluloid .	5 parts.
	Alcohol . .	50 ,,
	Camphor .	5 ,,
4.	Celluloid . .	5 ,,
	Amyl acetate .	50 ,,
5.	Celluloid . .	5 ,,
	Amyl acetate .	25 ,,
	Acetone . .	25 ,,

The Cie générale de Chromolithographie of Paris makes celluloid varnish from spongy celluloid as follows:—

The celluloid is placed in a vacuum, so that the alcohol and camphor evaporate—the damp mass can also be perforated and then dried. This porous celluloid dissolves readily. It is digested first with acetic ether and acetic acid, then with ether, with a mixture of alcohol and castor oil, and finally with a mixture of oil of turpentine, alcohol and amyl acetate. The resulting varnish can be used cold.

Hall prepares varnish from nitro-cellulose by dissolving 2½ lb. of pyroxylin in 4 gallons of amyl acetate and 4 gallons of coal-tar benzol. Wilson dissolves nitro-cellulose in amyl acetate, and another recipe gives 1 part of collodion wool to 6-7 of dinitrotoluol. Tscheuschner dissolves nitrated vegetable fibres in ether-alcohol containing boric acid; and zinc chloride dissolved in hydrochloric acid is also said to be a medium for celluloid varnish.

The following proportions will yield good varnishes:—

Nitro-cellulose	100	100 parts.
Amyl acetate	150	150 ,,
Amyl alcohol	150	400 ,,

Or 1 part of pyroxylin dissolved in 40 of an alcoholic solution of camphor diluted with iodoform.

Methyl alcohol	32 parts.
Amyl butyl or propyl acetate	18 ,,
Amyl alcohol	32 ,,
Soluble pyroxylin	5 ,,

Methyl alcohol	44 ,,
Amyl ,,	10 ,,
Propyl or butyl alcohol	20 ,,
Camphor	5 ,,
Soluble pyroxylin	10 ,,

BOLTON'S RECIPE.

Papyroxyl	30 parts.
Camphor	10 ,,
Alcohol	1,000 ,,

When collodion wool is used, 10 parts of the dry wool are suffused with 35 of ether, followed by 60 of 95 per cent. alcohol. The sediment is removed and 4-6 parts of camphor are stirred into the clear solution.

ECKSTEIN'S RECIPE.

Collodion wool	8-10 parts.
Ether or alcohol	100 ,,
Castor oil	2-4 per cent.
Resin	4-10 ,,

Celluloid bottle varnish is made by dissolving—

Pyroxylin	3-4 parts.
Boric acid	1 ,,
Resin	25 ,,
Pigment	50 ,,
Ether-alcohol	100 ,,

Gérard's patent prescribes dissolving 1 part of gelatine and 2 of trinitro-cellulose in 3 of glacial acetic acid, 19 parts of acetic acid, a little glutin, castor oil and gum-lac being added. American patent 371,021 gives a mixture of amyl chloride, acetate and chloracetate as solvent for pyroxylin; No. 372,100 mentions amyl chloride and camphor. A. M. Dougal's English patent states that a good celluloid varnish for leaden water-pipes is obtained by dissolving nitro-cellulose in alcohol and ether and adding castor oil or Canada balsam to the solution. A little magnesia or strontia can be added to increase the strength. Camphor phenols are also said to furnish good celluloid varnishes.

According to the nature of the solvents used, the solutions can be readily stained with coal-tar dyes dissolved in spirit or oil, and very pretty effects can be obtained in this way. Though it would be desirable to replace these volatile and inflammable solvents by safer ones, there does not seem much likelihood of this being done.

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